

**PHASE 2 REPORT - REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS
VOLUME 2C-A LOW RESOLUTION SEDIMENT CORING REPORT
ADDENDUM TO THE DATA EVALUATION AND INTERPRETATION REPORT
HUDSON RIVER PCBs REASSESSMENT RI/FS**

JULY 1998



For

**U.S. Environmental Protection Agency
Region II
and
U.S. Army Corps of Engineers
Kansas City District**

**Volume 2C-A
Book 1 of 2**

TAMS CONSULTANTS, Inc.

Gradient Corporation

TETRA TECH, INC.



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 2
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NEW YORK, NY 10007-1866

JUL 23 1998

To All Interested Parties:

The U.S. Environmental Protection Agency (EPA) is pleased to release the Low Resolution Coring Report for the Hudson River PCBs Superfund site. This report presents findings based on the analysis of the low resolution sediment core data collected by EPA in 1994 for the Reassessment. As part of this report, the 1994 sediment data is compared to sediment data previously collected by the New York State Department of Environmental Conservation in 1984 and 1976 - 1978.

The Low Resolution Coring Report, Volume 2C-A, is an addendum to the Data Evaluation and Interpretation Report, Volume 2C, which was released in February 1997. Combined, these volumes are considered the third report in the series of six reports that will make up the Phase 2 Report of the Reassessment. The Phase 2 Report was divided into sections at the request of members of the community interaction program, thereby allowing interested parties to comment on the reports prior to the incorporation of the work into the risk assessments and the feasibility study. It also separates the Phase 2 Report into more manageable individual documents.

As with the previous Phase 2 Reports, it is important to recognize that the conclusions in this report, although significant, do not indicate whether or not remedial action is necessary for the PCB-contaminated sediments of the upper Hudson. The numerical analysis (computer modeling) of fate and transport of PCBs, the associated ecological and human health risk assessments, and a feasibility study must be completed before any such conclusion can be reached.

EPA will accept comments on the Low Resolution Coring Report until **Monday, August 31, 1998**. Comments should be marked with the name of the report and should include the report section and page number for each comment. Comments should be sent to:

Douglas Tomchuk
USEPA - Region 2
290 Broadway - 20th Floor
New York, NY 10007-1866

Attn: LRC Comments

EPA will present the findings of this report as well as the Scope of Work for the Human Health Risk Assessment at a joint liaison group meeting in Albany, New York. Notification of this meeting was sent to liaison group members several weeks prior to the meeting. In the interim, between the release of this report and the end of the comment period, EPA will hold two public availability sessions to further answer public questions regarding the Low Resolution Coring Report and the Scope of Work for the Human Health Risk Assessment. These sessions will be

held on Wednesday, August 19, 1998 at the Holiday Inn Express in Latham, New York from 2:30 to 4:30 p.m. and from 6:30 to 8:30 p.m., and on Thursday, August 20, 1998 from 6:30 to 8:30 p.m. at Marist College in Poughkeepsie, New York.

If you need additional information regarding this report, the availability sessions or with respect to the Reassessment in general, please contact Ann Rychlenski, the Community Relation Coordinator for this site, at (212) 637-3672.

Sincerely yours,

A handwritten signature in black ink, appearing to be 'R. Caspe', followed by a long horizontal line extending to the right.

Richard L. Caspe, Director
Emergency and Remedial Response Division

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LOW RESOLUTION SEDIMENT CORING REPORT

EXECUTIVE SUMMARY

This report presents the findings from the analysis of data relating to the low resolution sediment coring program for the Hudson River PCBs Site Reassessment Study. The low resolution sediment coring program was designed to evaluate changes in sediment PCB inventory over time and the degree of burial of PCB-contaminated sediments.

Low resolution coring refers to the relative thickness of the sediment slices analyzed during the sampling program. In the low resolution coring program, the average thickness of a sediment slice was 9 inches (22 cm), compared to the 0.8-inch (2 cm) to 1.6-inch (4 cm) slices analyzed in the high resolution coring program.

BACKGROUND - The Low Resolution Sediment Coring Report is a companion to the Data Evaluation and Interpretation Report, which was issued in February 1997. Similar to the Data Evaluation and Interpretation Report, the Low Resolution Sediment Coring Report is based on geochemical analysis. However, whereas the Data Evaluation and Interpretation Report primarily evaluated the transport of PCBs through the analysis of water-column data and dated sediment cores, the Low Resolution Sediment Coring Report assesses the inventory of PCBs found in the Upper Hudson River sediments. The geochemical analysis in these reports will be complemented and verified to the extent possible by additional numerical analysis (*i.e.*, computer modeling). Results of the computer modeling will be reported in the Baseline Modeling Report, to be released in May 1999. In addition, the Low Resolution Sediment Coring Report does not explore the biological uptake and human health impacts, which will be evaluated in future Reassessment documents.

The Reassessment Remedial Investigation and Feasibility Study is being conducted by the U.S. Environmental Protection Agency in order to determine an appropriate course of action to address the PCB-contaminated sediments in the Upper Hudson River. This study is a reassessment of the Agency's interim "no-action" decision made in 1984. During the first phase of the Reassessment, EPA compiled existing data on the site and conducted preliminary analyses of the data. As part of the second phase, EPA conducted field investigations to characterize the nature and extent of PCB contamination in the Upper Hudson. The Phase 2 data, along with data from other sources, has been used to better understand the fate and transport of PCB contamination in the river.

Two large-scale sediment investigations were previously conducted by the New York State Department of Environmental Conservation (NYSDEC) to characterize the extent and magnitude of PCB contamination in the sediments--one from 1976 to 1978, and one in 1984. On the basis of data gained from these investigations, approximately forty zones of highly contaminated sediments, designated as *hot spots*, were identified. These data were used to estimate total PCB inventory in Hudson River sediments at the time of the completion of both the 1976-1978 and 1984 studies.

OBJECTIVES - The low resolution sediment coring program, conducted in July and August 1994, had two main objectives:

- Obtain new estimates of sediment PCB inventories at selected locations in the Thompson Island Pool to compare against the existing PCB sediment database constructed from the 1984 NYSDEC survey; and

- Refine the PCB mass estimates for a limited number of historic *hot spot* locations defined by the 1976-1978 NYSDEC survey in the Upper Hudson below the Thompson Island Dam.

Low resolution sediment coring was performed to examine PCB contamination in a limited number of areas and to augment and improve estimates of the sediment inventory and spatial distribution of PCBs previously developed for these areas. The comparison of previous surveys to current conditions is significant to the Hudson River PCBs Reassessment because changes in PCB inventories can indicate areas of the river where PCBs are being lost and/or gained.

In the Thompson Island Pool, locations for most of the cores were selected by grouping the samples into zones with minimal local sediment heterogeneity, thereby minimizing uncertainties due to factors other than PCB inventory changes. It was then possible to compare the 1994 data to the 1984 NYSDEC data and support general conclusions regarding PCB inventory change in the Thompson Island Pool. The coring locations below the Thompson Island Dam were selected to generate PCB mass estimates for areas which, based on previous estimates, represented approximately 75 percent of the *hot spot* inventory below the dam. It is inappropriate to extrapolate the inventory changes in those *hot spots* to other areas below the Thompson Island Dam. Other locations sampled were selected to characterize near-shore sediments.

ANALYTICAL TOOLS - Low resolution sediment core samples were analyzed on a congener-specific basis for PCBs, which allows for the same type of analysis of dechlorination products as was conducted for the Data Evaluation and Interpretation Report. In addition, radionuclide analyses of the isotopes cesium-137 and beryllium-7 in sediments were conducted. Beryllium-7 data were used to determine whether the top of the core showed evidence of recent deposition. The cesium-137 data were used to establish that the core had penetrated all post-1954 sediment, which correlates to the PCB-containing sediments. The radionuclide data allowed the low resolution cores to be assessed for completeness, because the absence of cesium-137 in the bottom of the core was a reliable indicator that the core did not miss any PCBs at depth (*i.e.*, the core was *complete*). Because the 1994 inventories are from cores that were determined to be complete, and because the previous inventories did not utilize radionuclide analyses and therefore may have been underestimated, the observed losses in PCB inventory are minimum estimates. Likewise, the observed gains in PCB inventories in certain areas are maximum estimates.

Major Findings - The analyses presented in the Low Resolution Sediment Coring Report lead to four major findings as follows:

1. From 1984 to 1994, in the Thompson Island Pool, there has been a net loss of approximately 40 percent of the PCB inventory in sediments which have concentrations typical of *hot spot* sediments.
2. There was little evidence found of widespread burial of PCB-contaminated sediment by clean sediment in the Thompson Island Pool. Burial is seen at some locations, but more core sites showed loss of PCB inventory than showed PCB gain or burial.
3. The PCB inventory for *Hot Spot* 28 calculated from the low resolution coring data is considerably greater than previous estimates. This apparent “gain” in inventory is attributed to significant underestimates in previous studies rather than actual deposition of PCBs in *Hot Spot* 28

4. From 1976-1978 to 1994, in the Upper Hudson below the Thompson Island Dam, there has been a net loss of PCB inventory in *hot spot* sediments sampled in the low resolution coring program.

These conclusions are briefly described and explained below.

1. **From 1984 to 1994, in the Thompson Island Pool, there has been a net loss of approximately 40 percent of the PCB inventory in sediments which have concentrations typical of *hot spot* sediments.** Sediments in the Thompson Island Pool with total PCB inventories of greater than 10 g/m² (typical of *hot spot* sediments) exhibit a statistically significant loss of PCBs. This inventory loss includes loss to the overlying water column as well as dechlorination. Specifically, there has been roughly a 30 percent decline in inventory due to actual loss from the sediments (from erosion, diffusion, groundwater advection, or other mechanisms) and a 10 percent loss via dechlorination. When the 30 percent loss is combined with an average dechlorination loss of approximately 10 percent, the result is a total PCB inventory loss of approximately 40 percent.

The PCBs lost from *hot spot* areas enter the water column and may be available to the food chain or deposited in other areas.

2. **There was little evidence found of widespread burial of PCB-contaminated sediment by clean sediment in the Thompson Island Pool. Burial is seen at some locations, but more core sites showed loss of PCB inventory than showed PCB gain or burial.** Thirty percent of coring sites do not exhibit burial, or may exhibit erosion, based on the absence of beryllium-7 in core tops. Comparisons of sediment core profiles between the 1984 and 1994 data indicate that burial is not occurring at more than half of the locations investigated. Burial does occur at some *hot spot* areas, but there is also evidence of sediment PCB loss occurring, often within the same *hot spots*. Again, there is more evidence for sediment PCB loss rather than burial.

Beryllium-7 is a naturally-occurring isotope whose presence in sediments indicates recent deposition or interaction with surface waters within the six months prior to sample collection. The absence of beryllium-7 was shown to be a statistically significant indicator of inventory loss. Absence of beryllium-7 is attributed to a core collected in a non-depositional area or an area that has undergone scour (erosion) of river sediment. Thus, this radionuclide was used to test a core top (0 to 1-inch) for the presence of recently deposited sediment. Surficial sediments in which beryllium-7 was not detected (no burial) had lower PCB inventories than cores in which beryllium-7 was detected, indicating that burial of PCB mass by less contaminated sediments is **not** occurring at these locations. Although this analysis does not offer proof of sediment scour, it does show that burial of contaminated sediments is not occurring in at least 30 percent of the coring sites.

The core profiles, or core results presented by depth, show an important finding. PCB maxima are principally found in the top-most core layer in approximately 60 percent of the samples, which represent shallow sediment (median core segment depth of 9 inches). These results indicate that burial of PCB-bearing sediments is not occurring on an extensive basis and that high concentrations of PCBs remain relatively close to the sediment/water interface.

In addition, the average depth to the maximum total-PCB concentration (taken as the bottom of the core section in which the PCB maximum was found) varied considerably according to whether the area showed a gain or loss of PCB inventory. In the *hot spots*, for cores exhibiting a PCB inventory increase, the average depth to the maximum total-PCB concentration was 18.7- inches (46.8-cm),

contrasted to 10.6 inches (26.5-cm) in the cores exhibiting a loss of PCB inventory. The difference in mean depth between areas of PCB loss and gain is statistically significant. This finding confirms that the PCB-maximum moves downward in areas of PCB (and accordingly, sediment) gain, and does not exhibit such burial in areas where PCB loss is occurring.

3. The PCB inventory for *Hot Spot 28* calculated from the low resolution coring data is considerably greater than previous estimates. This apparent “gain” in inventory is attributed to significant underestimates in previous studies rather than actual deposition of PCBs in *Hot Spot 28*. An evaluation of the 1994 data collected for the low resolution coring program found that the PCB inventory in *Hot Spot 28* was substantially greater than had been estimated in previous studies. The Low Resolution Sediment Coring Report estimates the mass of PCBs in *Hot Spot 28* to be 20 metric tons. Previous estimates varied between two to seven metric tons. Therefore, based on a comparison of these estimates there would appear to be a large gain in PCB inventory. However, further examination of the core profiles for *Hot Spot 28* shows that less than 50 percent of the sample locations have evidence of deposition (burial). The remaining sites are either unchanged or have undergone scour based on the presence of the maximum total-PCB concentration in the shallow sediment. The deposition history recorded by the high resolution cores indicates that this type of profile can only be caused by scour. Only between two to five percent of PCB mass was deposited between 1977 and 1991 for two nearby high resolution cores, thus making such a large gain in inventory unlikely. Therefore, the apparent “gain” of PCBs in *Hot Spot 28* based on a comparison of historical estimates to the current estimate is not real. There have been losses of PCBs from several locations within the hot spot and, overall, the *hot spot* represents no significant change in inventory. The previous mischaracterization of the inventory probably results from an initial inaccurate assessment of *Hot Spot 28* by the 1976-1978 sediment survey caused by too many shallow cores and grabs (*i.e.*, “incomplete” cores). EPA’s current estimate is based on cores that have been found to be “complete” based on radionuclide analysis.

4. From 1976-1978 to 1994, in the Upper Hudson below the Thompson Island Dam, there has been a net loss of PCB inventory in *hot spot* sediments sampled in the low resolution coring program. When the 1994 total PCB inventory is compared to the 1976-1978 inventory, a statistically significant loss of 50 to 80 percent of PCB inventory is seen for *Hot Spots 31, 34 and 37*. This represents a potential loss of approximately 3 metric tons into the water column, although some loss may be due to dechlorination. The other *hot spots* evaluated either appear unchanged or have not experienced significant gains in PCB inventory, with the exception of *Hot Spot 28*, as noted above.

Hot Spot 39 exhibits burial. Total-PCB concentrations are at greater depths than previous sediment surveys. Because of the inability to obtain “complete” cores in this *hot spot*, there is uncertainty in our current estimate as well as the previous estimates, making it difficult to determine whether there is inventory loss or gain. Given this uncertainty, *Hot Spot 39* is considered to not have experienced a significant change in inventory.

The sediment inventories of three areas appear unchanged (*Hot Spots 25, 35 and dredge location 182*), but only one (*Hot Spot 25*) had a sufficient number of samples to confirm the lack of change.

It should be noted that the calculations for *Hot Spots 28 and 39* show large PCB inventories of 20 and 4 metric tons, respectively. This is greater than the inventory of the entire Thompson Island Pool, which was estimated to be between 14.5 and 19.6 metric tons in the Data Evaluation and Interpretation Report, based on the 1984 NYSDEC data.

Overall, *hot spot* sediments below the Thompson Island Dam exhibit both losses and gains between 1976-1978 and 1994. Losses total a minimum of 3 metric tons. Apparent gains in certain *hot spots* were likely due to previously inaccurate estimates.

ADDITIONAL FINDINGS - There has been a net gain of PCB inventory in areas of the Thompson Island Pool outside of the *hot spots*. The additional PCBs may have come from redistribution of PCBs from high concentration areas or from PCBs that entered the pool from upstream sources, such as the GE Hudson Falls Plant site. Sediments with total PCB inventories of less than 10 g/m² exhibit a statistically significant gain of PCBs. However, this net gain is found at a limited number of locations, insufficient to support such a finding for all non-cohesive (coarse-grained) sediments in the Thompson Island Pool. The increase of PCB inventory in the Thompson Island Pool outside of the *hot spots* has an upper bound of approximately 100 percent, although the actual gain is probably much less.

Comparison of the river bottom texture type indicated by the side-scan sonar images with the 1976-1978 NYSDEC sediment survey grain-size data resulted in good agreement with one another. This indicates that side-scan sonar can be used to classify large areas of the river bottom in terms of sediment properties and that the river bottom depositional types remained constant. The comparison between side-scan sonar results and PCB levels in shallow sediments implies that side scan sonar images can be used to estimate both shallow sediment PCB concentrations and PCB inventories. *Hot spot* boundaries appeared accurate, although in some instances *hot spot* areas needed to be increased to include all nearby areas of high contamination.

Historical estimates of PCB mass in *hot spots* below the Thompson Island Dam assumed a solid specific weight of 1 g/cc . Based on the low resolution core relationship between solid specific weight and total PCB concentration, more appropriate values of solid specific weight ranged from 0.5 to 0.79 g/cc for the majority of the 1976-1978 *hot spot* sample locations. Applying a solid specific weight based on length weighted average concentrations yielded about a 20 to 30 percent decrease in the original PCB inventory estimates. In other words, the previous calculations of PCB inventories were somewhat overestimated.

Sediments in the near shore environment, which was defined as within 50 feet of the shoreline, had higher PCB concentrations than estimated in the Phase 1 Report. The Phase 1 Report estimated an exposure point concentration of 66 mg/kg (parts per million) for the 95 percent confidence interval of the arithmetic mean of the shall sediment concentration based on the 1984 data, whereas the current estimate would be within the range of 135 to 264 mg/kg. Implications of this change will be addressed in the swimming or wading exposure scenario in the Human Health Risk Assessment.

SUMMATION - The decrease in PCB inventories in the more contaminated sediments of the Thompson Island Pool and from several of the studied *hot spots* below the Thompson Island Dam, along with the indication of an inventory gain in the coarse sediments of the Thompson Island Pool, indicate that PCBs are being redistributed within the Hudson River system. These results show that the stability of the sediment deposits cannot be assured.

Burial of contaminated sediment by cleaner material is not occurring universally. Burial of more PCB-contaminated sediment by less contaminated sediment has occurred at limited locations, while significant portions of the PCB inventories at other *hot spots* have been re-released to the environment. It is likely that PCBs will continue to be released from Upper Hudson River sediments.

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ACRONYMS

ASTM	American Society for Testing and Materials	NYSDEC	New York State Department of
⁷Be	Beryllium-7		Environmental Conservation
cm	Centimeter	PCB	Polychlorinated Biphenyl
¹³⁷Cs	Cesium-137	PPB	Parts per Billion
DEIR	Data Evaluation and Interpretation Report	PPM	Parts per Million
DN	Digital Number	QA	Quality Assurance
ECD	Electron Capture Detector	QAPjP	Quality Assurance Project Plan
GC	Gas Chromatograph	RPD	Relative Percent Difference
GE	General Electric	RRT	Relative Retention Time
IQD	Interquartile Distance	RSD	Relative Standard Deviation
ITD	Ion Trap Detector	s	Standard Deviation (also as SD)
kg	Kilogram	SAP	Sampling and Analysis Plan
kHz	Kilohertz	SAS	Special Analytical Services
LQ	Lower Quartile	SOP	Standard Operating Procedure
LWA	Length-Weighted Average	SSW	Solid Specific Weight
MDPR	Molar Dechlorination Product Ratio	TC	Total Carbon
MPA	Mass Per Unit Area	TCL	Target Compound List (Organics)
MPI	Malcolm Pirnie, Inc.	TI	Thompson Island
MW	Molecular Weight	TKN	Total Kjeldahl Nitrogen
NPDES	National Pollution Discharge Elimination System	TN	Total Nitrogen
		TOC	Total Organic Carbon
		UQ	Upper Quartile
		USGS	United States Geological Survey

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GLOSSARY

<u>PARAMETER:</u>	<u>DEFINITION</u>
Arithmetic Mean	The sum of values divided by the number of values.
ASTM	The sieve and hydrometer-based grain size distribution analysis. This analysis is a modified version of ASTM Methods D421-85 and D422-63.
⁷ Be	Radioisotope Beryllium 7 (pCi/Kg).
Box & Whisker Plot	A plot which enables the quick examination of a number of variables and extraction of the major characteristics including the median, upper and lower quartiles, interquartile distance and outliers.
Bulk density	The mass of water and solids per unit volume of sediment (g/cc).
BZ#	The PCB congener nomenclature system developed by Ballschmiter & Zell (1980).
C/N	Total Carbon to Total Nitrogen Ratio (molar).
Chow's F test	Chow's F test (Fisher, 1970) addresses the hypotheses that the parameters have or have not changed between regressions developed for two data sets. It is developed by calculating error sum of squares or sum of squared residuals (SSEs) for regression models on each of the data sets individually and an SSE for a regression on the pooled data. The comparison is made by forming an <i>F</i> statistic with <i>k</i> and (<i>t</i> ₁ + <i>t</i> ₂ - 2 <i>k</i>) degrees of freedom, formed as (Kennedy, 1979) in which

$$F = \frac{[SSE (constrained) - SSE (unconstrained)] / k}{SSE (unconstrained) / (t_1 + t_2 - 2k)}$$

<i>SSE(unconstrained)</i>	=	the sum of the <i>SSE</i> s from the two separate regressions,
<i>SSE(constrained)</i>	=	the <i>SSE</i> from the regression on the pooled data,
<i>t</i> ₁	=	the number of observations in the first sample set,
<i>t</i> ₂	=	the number of observations in the second sample set, and
<i>k</i>	=	the number of parameters in the model, including the intercept term.

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	The resulting statistic can then be compared to a tabulation of the F distribution with k and $(t_1 + t_2 - 2k)$ degrees of freedom to test the hypothesis that parameters have changed significantly between data sets 1 and 2.
Clay %	Percent Clay - ASTM Classification by Laser Analysis (%).
Coarse Sand%	Percent Coarse Sand - ASTM Classification by Laser or Sieve Analysis (%).
Congener	The 209 different configurations of a PCB molecule resulting from multiple combinations of hydrogen, chlorine and position on the biphenyl molecule (two benzene rings linked at a single point).
^{137}Cs	Radioisotope Cesium 137 (pCi/Kg).
DEIR	Data Evaluation and Interpretation Report.
Delta ₈₄	The total PCB mass/area in 1994 minus the total PCB mass/area in 1984 divided by the total PCB mass/area in 1984.
d(x)	A grain-size distribution measure. The effective diameter of a theoretical sieve that would retain X percent of the sample. Equally the effective diameter that is larger than (100 - X) percent of a sample. Values for X are 10, 20, 30, 40, 50, 60, 70, 80, 90, or 99.
DN	Digital acoustic signal values of the 500 kHz sonar images. Each pixel of the side scan sonar images has a number assigned according to the shade of grey with values ranging from 0 to 255. The mean value of the assigned values in a region is the DN.
Fine Sand%	Percent fine sand - ASTM Classification by Laser or Sieve Analysis (%).
Fines	Percent fines by ASTM Analysis - ASTM Classification (%). Corresponds to the sum of clay and silt fractions by Laser analysis.
Geometric Mean	The antilog of the sum of the log-transformed values divided by the number of values.
Geometric Mean Diameter	Antilog of the arithmetic mean of the logs of the diameters. See also mean phi. Mean diameter of mass weighted phi value (mm).
Gravel %	Percent Gravel - ASTM Classification by Laser or Sieve Analysis (%)

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Homologue	A grouping of PCB congeners based on the number of chlorine atoms on the molecule. A PCB molecule can have from one to ten chlorine atoms. The homologue groups are mono, di, tri, tetra, penta, hepta, hexa, octa, nona and deca.
HSD	Honestly significant difference. (See Tukey-Kramer HSD.)
Laser	Method for obtaining sediment grain size distribution. This method provides greater resolution of fines.
Mahanalobis Distances	Mahalanobis distances (SAS, 1994) are a means of determining outliers in a correlation analysis. The Mahalanobis distance from the multivariate mean (centroid) depends on estimates of the mean, standard deviation and correlation for the data. The points with the largest distances are the multivariate outliers. For each observation number the distance is denoted and computed as:

$$d_i = \sqrt{(a_i - \bar{a})' S^{-1} (a_i - \bar{a})}$$

where:

a_i is the data for the i th row

\bar{a} is the row of means

S is the estimated covariance matrix for the data

and $(a_i - \bar{a})'$ is the transpose of $(a_i - \bar{a})$ matrix.

The distances are then compared to a reference distance determined by

$$\sqrt{F * n_v}$$

where:

n_v is the number of variables

and F is a statistic with parameters including 95% confidence level, $n_v / (n - n_v - 1)$ degrees of freedom, and is centered at zero.

(n =number of observations)

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If any of the distances are further from the center than the reference distance they are considered outliers. With the jackknife method, d_i is calculated without including the i th observation in the mean, standard deviation or correlation matrix. In this case, outliers cannot distort the estimates of means or covariance.

MDPR Molar Dechlorination Product Ratio is the ratio of the sum of five congener molar concentrations (BZ# 1, 4, 8, 10, and 19) to the total sample molar concentration.

MPA The PCB mass per unit area. The MPA was calculated from the product of the concentration of PCBs (mg/kg), length (m) and density (kg/m³).

$$MPA = \sum_{i=1}^n C_i * L_i * r_i$$

MPA₃₊ The Tri+ mass per unit area. The MPA₃₊ was calculated from the product of the concentration of Tri+(mg/kg), length (m) and density (kg/m³).

$$MPA = \sum_{i=1}^n C_{Tri+i} * L_i * r_i$$

MW The fractional difference in the mean molecular weight relative to Aroclor 1242.

Mean Phi Mass weighted mean phi value (phi). The inverse log (base 2) of this value is the geometric mean diameter.

Median The data value located halfway between the smallest and largest values.

Median Diameter The diameter in a grain size distribution located halfway between the smallest and largest values.

Medium Sand% Percent medium sand ASTM classification by Laser or ASTM Analysis (%).

Non-target One of the additional 36 congeners reported in the Phase 2 data set. Reported values may or may not be calibrated.

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<u>PARAMETER:</u>	<u>DEFINITION</u>
NYSDEC	New York State Department of Environmental Conservation..
Particle density	Sediment particle density (g/cc).
Percent Similarity	A means of comparing grain size distributions. The lower value for each of the grain size parameters is summed. The closer the sum is to 100% the more similar the distributions are.
Percent Solids	Mass of solids per unit mass of wet sediment. Max value = 100%.
Phi -0.5	Mass fraction with a diameter larger than -0.5 phi and smaller than -1.0 phi (%).
Phi -1.0	Mass fraction with a diameter larger than -1.0 phi and smaller than -1.5 phi (%).
Phi -1.5	Mass fraction with a diameter larger than -1.5 phi and smaller than -2 phi (%).
Phi -2.0	Mass fraction with a diameter larger than -2 phi (%).
Phi 0.0	Mass fraction with a diameter larger than 0.0 phi and smaller than -0.5 phi (%).
Phi 0.5	Mass fraction with a diameter larger than 0.5 phi and smaller than 0.0 phi (%).
Phi 1.0	Mass fraction with a diameter larger than 1.0 phi and smaller than 0.5 phi (%).
Phi 1.5	Mass fraction with a diameter larger than 1.5 phi and smaller than 1.0 phi (%).
Phi 2.0	Mass fraction with a diameter larger than 2.0 phi and smaller than 1.5 phi (%).
Phi 2.5	Mass fraction with a diameter larger than 2.5 phi and smaller than 2.0 phi (%).
Phi 3.0	Mass fraction with a diameter larger than 3.0 phi and smaller than 2.5 phi (%).
Phi 3.5	Mass fraction with a diameter larger than 3.5 phi and smaller than 3.0 phi (%).
Phi 4.0	Mass fraction with a diameter larger than 4.0 phi and smaller than 3.5 phi (%).
Phi 4.5	Mass fraction with a diameter larger than 4.5 phi and smaller than 4.0 phi (%).
Phi 5.0	Mass fraction with a diameter larger than 5.0 phi and smaller than 4.5 phi (%).

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<u>PARAMETER:</u>	<u>DEFINITION</u>
Phi 5.5	Mass fraction with a diameter larger than 5.5 phi and smaller than 5.0 phi (%).
Phi 6.0	Mass fraction with a diameter larger than 6.0 phi and smaller than 5.5 phi (%).
Phi 6.5	Mass fraction with a diameter larger than 6.5 phi and smaller than 6.0 phi (%).
Phi 7.0	Mass fraction with a diameter larger than 7.0 phi and smaller than 6.5 phi (%).
Phi 7.5	Mass fraction with a diameter larger than 7.5 phi and smaller than 7.0 phi (%).
Phi 8.0	Mass fraction with a diameter larger than 8.0 phi and smaller than 7.5 phi (%).
Phi 8.5	Mass fraction with a diameter larger than 8.5 phi and smaller than 8.0 phi (%).
Phi 9.0	Mass fraction with a diameter larger than 9.0 phi and smaller than 8.5 phi (%).
Phi 9.5	Mass fraction with a diameter larger than 9.5 phi and smaller than 9.0 phi (%).
Phi 10.0	Mass fraction with a diameter larger than 10.0 phi and smaller than 9.5 phi (%).
Phi 10.5	Mass fraction with a diameter larger than 10.5 phi and smaller than 10.0 phi (%).
RPD	Relative Percent Difference is the absolute value of the difference between values divided by the average of the values.
Sand %	Percent Sand by Sieve Analysis - ASTM Classification (%).
Shallow Sediment	Sediment 0 - 12 inches below the sediment/water interface.
Shapiro and Wilk W Test	The W test (Gilbert, 1987) developed by Shapiro and Wilk (1965) is an effective method for testing whether a data set has been drawn from an underlying normal distribution. Furthermore, by conducting the test on logarithms of the data, it is an equally effective way of evaluating the hypothesis of a lognormal distribution. The W test compares the range of values to the number and mean of the samples collected to assess the probability of an underlying normal distribution. The hypothesis that the underlying distribution is normal is rejected at the 95% confidence level.

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$$W = \frac{\sum_{i=1}^k a_i (x_{[n-i+1]} - x_{[i]})}{\sum_{i=1}^n (x_i - \bar{x})^2}$$

where:

x_i = data drawn at random from some population
 k = n/2 if n is even
 = (n-1)/2 if n is odd
 a_i = coefficient for the Shapiro-Wilk test dependent on n

Silt Percent	Percent Silt - ASTM Classification by Laser Analysis (%).
Skewness	Statistical characterization of the degree of asymmetry of the phi values about the phi class mean - Laser Analysis (Unitless).
Solids specific weight	Sediment solids specific weight (g/cc) i.e., mass of solids per unit volume of wet sediment.
Sorting	Standard deviation of the phi values - Laser Analysis (Unitless).
Surficial Sediment	Sediment 0 - 2 inches below the sediment/water interface.
Target Congener	One of the original 90 target congeners chosen for the Phase 2 investigation. Reported values are based on congener specific calibration and undergo data validation.
Theil's U Statistic	<p>Theil's U statistic, otherwise known as Theil's inequality coefficient (Theil, 1961), is often used for the evaluation of model simulation error. The U statistic gives a measure of the consistency between forecasts (e.g., Low Resolution predictions using the High Resolution model) and the data used to develop the forecasts. It ranges from 0 to 1, with 0 indicating perfect prediction. The variance of the U statistic can be approximated (for U less than 0.3) as U^2/T, where T is the number of samples in the "forecast".</p> <p>The U statistic is defined as (Pindyck and Rubinfeld, 1981)</p>

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$$U = \frac{\sqrt{\frac{1}{T} \sum_{t=1}^T (Y_t^s - Y_t^a)^2}}{\sqrt{\frac{1}{T} \sum_{t=1}^T (Y_t^s)^2 + \frac{1}{T} \sum_{t=1}^T (Y_t^a)^2}}$$

where:

Y_t^s = simulated value for observation t ,
 Y_t^a = actual value for observation t , and
 T = total number of observations.

The numerator of U is simply the root mean square simulation error, but the scaling of the denominator is such that U always falls between 0 and 1.

The U statistic may also be decomposed into portions attributed to bias or systematic error (U^m), variance or ability of the model to replicate the degree of variability in the variable of interest (U^s), and covariance or unsystematic error (U^c). These *proportions of inequality*, which sum to 1, are defined as:

$$U^M = \frac{(\bar{Y}^s - \bar{Y}^a)^2}{(1/T) \sum (Y_t^s - Y_t^a)^2}$$

where:

\bar{Y}^s = the mean of the series Y_t^s ,

$$U^S = \frac{(\mathbf{s}_s - \mathbf{s}_a)^2}{(1/T) \sum (Y_t^s - Y_t^a)^2}$$

\bar{Y}^a = the mean of the series Y_t^a ,

$$U^C = \frac{2(1 - \mathbf{r}) \mathbf{s}_s \mathbf{s}_a}{(1/T) \sum (Y_t^s - Y_t^a)^2}$$

\mathbf{s}_s = the standard deviation of the series Y_t^s ,

\mathbf{s}_a = the standard deviation of the series Y_t^a , and

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= the correlation coefficient of the two series.

When U is non-zero, a desirable evaluation of a model will show that the non-zero component is dominantly attributable to the covariance or unsystematic component, which represents non-controllable random variability. Weight on the bias component indicates that the linear relationship differs between the two data sets. Weight on the variance component indicates that the difference is attributable primarily to differing variances between the two data sets.

TI Dam Thompson Island Dam.

TI Pool The Thompson Island Pool is the segment of the Hudson River between Rogers Island and the Thompson Island Dam.

TKN Total kjeldahl nitrogen (mg/kg DW), a measure of organic nitrogen.

TOC Total organic carbon (percent DW).

Total PCBs The sum of the 126 congener concentrations used throughout the Phase 2 analysis.

Tukey-Kramer Honestly Significant Difference Tukey-Kramer HSD (Box et al., 1978) is used to calculate the confidence interval for $n_i - n_j$ when comparing k averages. Where n_j and n_i are the number of observations made when populations i and j were tested. The confidence limits for $n_i - n_j$ are given by:

$$(\bar{y}_i - \bar{y}_j) \pm \frac{q_{k,n,\alpha/2}}{\sqrt{2}} s \sqrt{\frac{1}{n_i} + \frac{1}{n_j}}$$

where:

\bar{y}_i = the average of the observations made in population i

k = the number of averages being compared

v = the degrees of freedom in the estimate s^2 of variance ²

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<u>PARAMETER:</u>	<u>DEFINITION</u>
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Tukey Kramer
Honestly Significant
Difference (Cont)

$q_{k,v}$	=	the appropriate upper significance level of the <i>studentized</i> range of k and v.
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Any difference in averages greater than the confidence limit calculated is considered to be significant. This formula is exact if the numbers of observations n in all the averages are the same, and approximate if the averages are based on unequal numbers of observations. Since the range statistic $q_{k,v}$ is used rather than the t statistic all possible comparisons of averages may be made and the size of the confidence interval for any given level of probability is larger. With a larger confidence interval statistically significant differences can be detected with greater certainty.

Tri+

The sum of trichloro to decachloro homologues.

1. INTRODUCTION

1.1 Purpose of Report

This volume is part of a series of reports describing the results of the Phase 2 investigation of the Hudson River sediment polychlorinated biphenyls (PCB) contamination. This report, entitled Phase 2 Volume 2C-A, The Low Resolution Coring Report - Addendum to the Data Evaluation and Interpretation Report, discusses the results from the Low Resolution Sediment coring Program and their interpretation. This investigation is being conducted under the direction of the United States Environmental Protection Agency (USEPA) as part of a three-phase Remedial Investigation and Feasibility Study (RI/FS) intended to reassess the 1984 No Action decision of the USEPA concerning sediments contaminated with PCBs in the Upper Hudson River. For purposes of the Reassessment, the area of the Upper Hudson River considered for remediation is defined as the river bed between the Fenimore Bridge at Hudson Falls (just south of Glens Falls) and the Federal Dam at Troy. Plate 1-1 presents a map of the general site location and the Hudson River drainage basin.

In December 1990, USEPA issued a Scope of Work for reassessing the No Action decision for the Hudson River PCB site. The scope of work identified three phases:

- Phase 1 - Interim Characterization and Evaluation
- Phase 2 - Further Site Characterization and Analysis
- Phase 3 - Feasibility Study

The Phase 1 Report (TAMS/Gradient, 1991) is Volume 1 of the Reassessment documentation and was issued by the USEPA in August 1991. It contains a compendium of background material, discussion of findings and preliminary assessment of risks.

The Final Phase 2 Work Plan and Sampling Plan (TAMS/Gradient, 1992a) detailed the following main data-collection tasks to be completed during Phase 2:

- High and low resolution sediment coring;
- Geophysical surveying and confirmatory sampling;

- Water column sampling (including transects and flow-averaged composites);
and
- Ecological field program.

The Database for the Hudson River PCBs Reassessment RI/FS, which is described in the Database Report (Volume 2A in the Phase 2 series of reports; TAMS/Gradient, 1995) provides the validated data for the Low Resolution Sediment Coring Report. USEPA issued Release 3.0 of the database on CD-ROM in March 1996. Subsequently, there have been several updates to the database. The Low Resolution Sediment Coring Report utilizes Release 3.5, which was updated in June 1997. Subsequent revisions of the Hudson River database, 3.6, 3.7, and 4.0, contain the same low resolution coring data as found in Release 3.5, with one exception. Releases 3.7 and 4.0 contain an additional parameter, sediment principal fraction, which was generated from the sieve and laser grain-size data as part of the preparation of this report. Release 4.0 of the Database for the Hudson River PCBs Reassessment RI/FS will be available in July 1998.

This report is Volume 2C-A in the series of Reassessment documents presenting results and findings of the Phase 2 characterization and analysis activities. It contains the results and findings of the 1994 low resolution coring program and provides a comparison to the 1976 to 1978 and 1984 New York State Department of Environmental Conservation (NYSDEC) sediment data.

1.2 Report Format and Organization

The information gathered and the findings of this phase are presented here in a format that is focused on answering questions critical to the Reassessment, rather than reporting results strictly according to Work Plan tasks. In particular, results are presented in a way that facilitates input to other aspects of the project. Chapter 2 describes the technical approach for the Low Resolution Coring Program, field sampling procedures, and sample analyses. Chapter 3 interprets the results of the program and presents evidence to show how the low resolution coring results build on previously collected Phase 2 data. The three subchapters of Chapter 3 cover: 1) a comparison of the low resolution coring program with high resolution core PCB results; 2) examination of correlations among the various low resolution core analyses; and 3) interpretation of low resolution core results along with the side-scan sonar data. Chapter 4 examines PCB inventories in the areas of study.

Sediment inventories estimated from the low resolution cores are compared with historical studies of the sediments conducted by NYSDEC in 1976 to 1978 and 1984.

This report is organized in two books. The first contains the document text and appendices. The second contains the figures, plates, and tables referenced throughout the main body of the report. Appendix tables are found at the end of each appendix section.

1.3 Project Background

1.3.1 Site Description

The Hudson River PCBs Superfund site encompasses the Hudson River from Hudson Falls (River Mile [RM] 198) to the Battery in New York Harbor (RM 0), a river distance of nearly 200 miles. Because of their different physical and hydrologic regimes, approximately 40 miles of the Upper Hudson River, from Hudson Falls to Federal Dam (RM 153.9), is distinguished from the Lower Hudson, from Federal Dam to the Battery.

1.3.2 Site History

Over a 30-year period ending in 1977, two GE facilities, one in Fort Edward and the other in Hudson Falls, NY, used PCBs in the manufacture of electrical capacitors. Various sources have estimated that between 209,000 and 1,300,000 pounds (95,000 to 590,000 kilograms [kg]) of PCBs were discharged between 1957 and 1975 from these two GE facilities (Sofaer, 1976; Limburg, 1984; Sanders, 1989). Discharges resulted from washing PCB-containing capacitors and PCB spills. Untreated washings are believed to have been discharged directly into the Hudson from about 1951 through 1973 (Brown *et al.*, 1984). No records exist on which to base estimates of discharges from the beginning of PCB capacitor manufacturing operations in 1946 to 1956; however, discharges during this period are believed to be less than in subsequent years. Discharges after 1956 have been estimated at about 30 pounds (14 kg) per day or about 11,000 pounds (5,000 kg) per year (Bopp, 1979, citing 1976 litigation; Limburg, 1986, citing Sofaer, 1976). In 1977, manufacture and sale of PCBs within the U.S. was stopped under provisions of the Toxic Substances and Control Act (TSCA). PCB use ceased at the GE facilities in 1975 and only minor discharges (about 0.5 kg/day

or less [Brown *et al.*, 1984; Bopp, 1979]) are believed to have occurred during facility shutdown and cleanup operations through mid-1977, when active discharges ceased. GE had been granted a National Pollutant Discharge Elimination System (NPDES) permit allowing up to 30 lbs/day to be discharged during this period (Sanders, 1989). According to scientists at GE, at least 80 percent of the total PCBs discharged are believed to have been Aroclor 1242, with lesser amounts of Aroclors 1254, 1221, and 1016. However, the Aroclors that were discharged varied over time, with Aroclor 1254 being 75 percent or more of the total until about 1955; Aroclor 1242 being at least 95 percent of the discharges from about 1955 through 1971; and Aroclor 1016 being close to 100 percent of the discharge from 1971 through 1977 (Brown *et al.*, 1984).

A significant portion of the PCBs discharged to the river adhered to suspended particulates and subsequently accumulated downstream as sediment as they settled in the impounded pool behind the former Fort Edward Dam (RM 194.8), as well as in other impoundments farther downstream. Because of the proximity to the GE discharges, sediments behind the Fort Edward Dam were probably among the most contaminated to be found in the Hudson, although this was not well known in the 1970s. Because of its deteriorating condition, the dam was removed in 1973. During subsequent spring floods, the highly contaminated sediments trapped behind the dam were scoured and transported downstream. A substantial portion of these sediments were stored in relatively quiescent areas of the river. These areas, which were surveyed by NYSDEC in 1976 to 1978 and 1984 have been described as PCB *hot spots*. Exposed sediments from the former pool remaining behind the dam site, called the "remnant deposits," have been the subject of several remedial efforts.

PCB releases from the GE Hudson Falls site near the Bakers Falls Dam through migration of PCB oil through bedrock has also occurred, although the extent and magnitude of this release are not well known. This release through bedrock continued until at least 1996, when remedial activities by GE brought the leakage under control. Despite some evidence for its existence prior to 1991 based on United States Geological Survey (USGS) data, this leakage was not identified until the partial failure of an abandoned mill structure near GE's Hudson Falls plant site in 1991. This failure caused a large release of what were probably PCB-bearing oils and sediments that had accumulated within the structure. This failure also served to augment PCB migration from the bedrock beneath the plant to the river until remedial measures by GE over the period 1993 to 1997 greatly reduced the release rate. A more in-depth discussion of PCB sources is contained in the Data Evaluation and Interpretation Report (DEIR; TAMS *et al.*, 1997).

1.4 Background for the Low Resolution Sediment Coring Program

Two previous large-scale sediment investigations were conducted by NYSDEC; one in 1976 to 1978 (reported in Tofflemire and Quinn, 1979), and one in 1984 (reported by Brown *et al.*, 1988). The 1976 to 1978 sampling covered the area from Fort Edward to Troy (RM 194.8 to RM 154); whereas the 1984 sampling was restricted to the Thompson Island (TI) Pool (RM 194.6 to RM 188.5). On the basis of data gained from these investigations, approximately 40 zones of high contamination, designated as *hot spots*, were identified. These data have been used to estimate total PCB inventory in Hudson River sediments (Tofflemire and Quinn, 1979; Brown *et al.*, 1988). As part of this investigation, the 1976 to 1978 and 1984 data have been subjected to more sophisticated mathematical evaluation (including a kriging analysis of the 1984 data) to develop detailed maps of contamination (TAMS *et al.*, 1997).

These surveys served to describe Upper Hudson sediment conditions at the time of their completion. An issue of great significance to the Hudson River PCBs Reassessment is the applicability of previous surveys to current conditions. To some degree, this issue was addressed by the geophysical surveying of the Upper Hudson as part of the Phase 2 investigation. This survey covered 31 of the 36 *hot spots* previously defined by NYSDEC. Although 40 *hot spots* were originally defined, four *hot spots* near Rogers Island were removed by dredging prior to 1980. As discussed in the DEIR (TAMS *et al.*, 1997), the geophysical survey documented the continued presence of fine-grained sediments in many of the areas previously defined as *hot spots*. This indicates that much of the PCB-contaminated sediment deposited from 1955 to 1978 is probably still in place. Nonetheless, a more direct assessment of the current PCB inventory still contained within the sediments was desired to confirm this finding.

The DEIR (TAMS *et al.*, 1997) discussed the results of several of the earlier Phase 2 investigations, including the high resolution coring program. The high resolution coring involved slicing each core into sections at two to four centimeter intervals to provide a detailed (*i.e.*, highly resolved) history of PCB deposition at the coring location. In contrast, the low resolution cores were sliced into three relatively thick sections at approximately 22 cm (9 in) intervals. These thickly sliced cores do not provide sufficient resolution to examine the depositional history at the coring site, hence

the term *low resolution*, but they do provide an excellent basis on which to estimate the sediment PCB inventory.

1.5 Low Resolution Sediment Coring Program Objectives

The Low Resolution Sediment Coring Program had two main objectives:

- 1) Obtain new estimates of sediment PCB inventories at a number of locations in the TI Pool to compare against the existing PCB sediment database constructed from the 1984 NYSDEC survey; and
- 2) Refine the PCB mass estimates for a limited number of historic *hot spot* locations defined by the 1976 to 1978 NYSDEC survey in the Upper Hudson below the TI Dam.

The implementation of the sampling program was based upon a review of the historic sediment records from NYSDEC, GE, and others, in conjunction with the results from the geophysical survey. The low resolution coring effort in the TI Pool was intended to establish the extent to which the sediment inventory calculated from the 1984 NYSDEC data (TAMS *et al.*, 1997) accurately reflected current conditions. The low resolution coring in the lower reaches of the Upper Hudson River (below the TI Dam) provided information to refine the accuracy of previous *hot spot* sediment PCB inventory estimates which were based on a relatively small number of samples (from 1976 to 1978), as well as providing a measure of the contribution of areas below the TI Pool to the Upper Hudson River sediment PCB inventory. It should be noted that the 1988 NYSDEC report indicated that "no major change in the distribution of PCBs in the bed of the TI Pool between 1977 and 1984 is evident" (Brown *et al.*, 1988), even though the PCB inventory reported by Brown *et al.* (1988) was less than half of the PCB mass estimated by Tofflemire and Quinn (1979). Brown *et al.* (1988) concluded "that most of the difference between 1977 and 1984 PCB mass estimates was due to differences in calculation methods and assumptions" after taking into account USGS estimates of PCB transport from Fort Edward to Schuylerville from 1978 to 1984 (Brown *et al.*, 1988).

Low resolution coring was performed to examine PCB contamination in a limited number of areas and to augment and improve estimates of the spatial distribution of PCBs initially developed

for these areas. The low resolution coring program was not intended to provide the extensive spatial coverage obtained as part of the earlier NYSDEC investigations. Rather, the program focused on obtaining information to be used in conjunction with the other Phase 2 sampling programs as well as to augment and update the data obtained in the prior NYSDEC surveys.

In the subsequent chapters, the following conventions are used concerning the description of sediments near the sediment/water interface and differentiate between the samples taken for the low and high resolution coring programs. *Shallow sediments* refer to sediments within 12 inches (30 centimeters [cm]) of the sediment/water interface. The top segment of each low resolution core, beginning at the sediment/water interface and extending down about 9 inches (22.5 cm), is considered to represent shallow sediments. *Surficial sediments* refer to sediments within 2 inches (5 cm) of the sediment/water interface. The top two slices of a high resolution core are considered to represent surficial sediments by this definition. Surficial sediment samples were also obtained for radionuclide analysis exclusively as part of the low resolution coring program. In order to obtain and refine the estimates of the entire sediment PCB inventory at each sampling location as described earlier in the objectives, low resolution core collection included both shallow and deeper sediments for analysis.

2. SAMPLING DESIGN AND METHODS

2.1 Technical Approach for the Low Resolution Sediment Coring Program

As discussed in Section 1.5, the Low Resolution Sediment Coring Program was designed with two basic investigation objectives. First, the program was to assess the current status of the sediment PCB inventory of the Thompson Island (TI) Pool relative to the NYSDEC survey completed in 1984. The second objective was to assess, to a limited degree, the sediment PCB inventory of several previously defined *hot spots* in the Upper Hudson below the TI Dam. Each of these objectives was focused on limited study areas so as not to repeat the earlier, more extensive surveys. In both cases, the intent was to provide a basis on which to assess the current applicability of the historical surveys.

The TI Pool was sampled intensively in 1984, with over 1,200 samples collected on a triangular grid with 125-foot centers. The spatial coverage of that effort was adequate for the purpose of estimating PCB sediment mass inventory, as discussed in Brown *et al.*, 1988 and TAMS *et al.*, 1997. Rather than resurvey the entire TI Pool, the 1994 low resolution coring effort focused on replicating a representative subset of the 1984 locations. The intent was to assess the comparability of the current PCB inventories at these locations relative to the 1984 conditions. Based on these comparisons, an assessment of the current applicability of the entire 1984 data set could be made. The locations sampled in the TI Pool as part of the low resolution coring program were grouped into 15 relatively small zones or clusters. Within these clusters, samples were collected as near as possible to the same locations sampled by NYSDEC in 1984. Each zone generally consisted of about four or five sampling points, corresponding to the original NYSDEC locations. The new results were then used to compare the current sediment PCB concentrations in the TI Pool with the previously determined ones. The analysis and comparison of these results are presented in the subsequent chapters of this report. In addition to the 15 clusters, four additional clusters were located in near-shore areas of fine-grained sediment where the original 1984 NYSDEC coverage was poor. These samples were intended to characterize near-shore sediment contamination. These near-shore locations represent potential human exposure routes

for direct sediment contact as well as a potentially important but an undocumented reservoir of PCBs.

The locations for re-sampling under this program were selected based on a review of the 1984 data. In order to assess the changes in sediment PCB inventory and avoid uncertainty due to variability stemming from causes other than PCB inventory changes, the sampling locations were grouped into selected zones with minimal local sediment heterogeneity. Sediment heterogeneity was evaluated based on the following information:

- 1984 PCB data, showing PCB inventories within each zone to be similar;
- Side-scan sonar data, establishing the presence of similar material within each zone; and
- Field logs or other observations made during the 1984 sampling and, where available, 1992 confirmatory coring data to verify similar sedimentological properties.

In general each sampling zone (cluster) consisted of three to six locations with similar sediment properties and PCB concentrations (expressed as mass per unit area, *e.g.*, g/m²) which typically varied by a factor of two or less, and no more than a factor of three. One "null set," that is a zone in which PCBs were previously reported as not detected, was also included in the low resolution coring program. A total of 19 clusters and 76 cores were collected from the TI Pool during the Low Resolution Sampling Program.

Below the TI Dam, the 1976 to 1978 NYSDEC sampling program identified 20 *hot spots*, numbered 21 to 40 (Tofflemire and Quinn, 1979). However, the spatial coverage of the 1976 to 1978 NYSDEC sampling was not as intensive as the 1984 survey so the areas of these *hot spots*, and the resulting PCB inventory estimates, were based on a relatively small number of samples. As part of the low resolution coring program, seven of these *hot spots* were re-sampled to determine the current PCB inventory. These data were designed to assess how well estimates based on the limited 1976 to 1978 data reflect the current extent and magnitude of PCB contamination. The *hot spots* selected for the low resolution coring program are those in which previous estimates have indicated the highest PCB inventories and which physically span a substantive length of the river. Based on the NYSDEC estimates, these *hot spots* represented about

74 percent of the total mass of PCBs in *hot spots* below the TI Dam. The spatial intensity of the low resolution coring effort in these areas (below the TI Pool) was adjusted so that the entire area previously identified as the zone of contamination was covered by seven to ten low resolution cores. In addition, four near-shore or exploratory locations were selected in this region in areas not covered by the 1976 to 1978 NYSDEC survey to examine sediment contamination in unstudied zones of fine-grained sediments.

The sample collection procedure used for the low resolution coring program was similar to that used for the high resolution coring program although there are important differences which are discussed later. The term *low resolution coring* arises from the subdivision of the cores. In general, low resolution cores were separated into 9-inch (22.5-cm) layers, as opposed to the 0.8 to 1.5-inch (2 to 4-cm) thick layers used in the high resolution coring program. However, since a goal of the low resolution coring program was to verify total PCB inventories, the thickness of the low resolution core slice was modified as necessary so that all of the apparently contaminated material is included in the samples submitted for PCB analysis from each core. "Apparently contaminated material" was determined by the field geologist, based on the depth to which wood chips or cellulose-type material were present in the core. In addition, core intervals were chosen to coincide with visible sediment horizons, such as a sand/silt boundary or a change in sediment color. Where applicable, the low resolution core length and sampling interval were made to correspond to the same lengths as the original NYSDEC sample at that station when no other sedimentological criteria could be used. The low resolution cores ranged in length from 6 to 54-inches (15 to 137-cm) of sediment. Cores were advanced through the sediment until the coring apparatus could not penetrate any further.

One to three core slices were obtained from each core for PCB analysis, typically representing a total of about 18 to 20-inches (45 to 50-cm) of sediment. Below the deepest layer analyzed for PCB contamination in each core, an additional 3-inch (7.5-cm) slice was collected for radionuclide analysis only. The results from this layer were used to verify that the core thickness was sufficient to recover all contaminated sediment deposition based on the discussion below.

One of the areas of uncertainty between the assumptions used for PCB mass estimates made by Tofflemire and Quinn (1979) and Malcolm Pirnie, Inc. (MPI, 1992) is the depth to which PCB contamination extends. In cores collected from throughout the Hudson, PCBs are first detectable

in strata deposited in the late 1940s to early 1950s, with concentrations increasing from the mid-1950s to a peak in the early 1970s (Bopp and Simpson, 1989; TAMS *et al.*, 1997). However, the contribution of PCBs from deposition prior to 1955 is relatively insignificant, as confirmed by the 1992 high resolution core data. Cesium-137 (^{137}Cs) has a similar release history, with the radionuclide first appearing in 1954 with the onset of atmospheric nuclear weapons testing, from which ^{137}Cs is derived. Given the coincidence of the PCB and ^{137}Cs histories in the 1950s, ^{137}Cs was analyzed in the deepest layer from each core. Absence of ^{137}Cs in this layer indicated that the core had been advanced to pre-1954 sediments and to a sufficient depth to account for all substantive PCB deposition.

2.2 Field Sampling

The low resolution sediment coring program was designed to further characterize and analyze site conditions at the Hudson River PCBs Superfund site. The low resolution sampling program took place from July 13, 1994 to August 12, 1994. The Phase 2B Sampling and Analysis Plan/Quality Assurance Project Plan Volume 4 (TAMS/Gradient, 1994) detailed the sample collection and analytical procedures, which are summarized below.

In addition to the interpretation of the low resolution sediment coring samples, this report also discusses the side-scan sonar results obtained in the earlier portion of the Phase 2 investigation. A detailed discussion of the side-scan sonar program can be found in the DEIR (TAMS *et al.*, 1997) while a brief description is provided here. Side-scan sonar data covering the Upper Hudson from above Bakers Falls to Lock 5 were collected in 1991 and 1992. Essentially, acoustic signals (digitally recorded sound) were used to create false-color grey-scale images of the river bottom. These images were then combined to form mosaic maps of the river bottom wherein brighter areas on the images corresponded to coarser-grained sediments and darker areas corresponded to finer-grained sediments. The sediment classifications as defined by the side-scan sonar images were compared to low resolution coring grain size data. These data are discussed in Section 3.3 of this report. The comparison of the side-scan sonar results to previous sediment collection efforts (confirmatory sampling) is described in the DEIR (TAMS *et al.*, 1997).

2.2.1 Sample Locations

Low resolution sediment coring was conducted in the Upper Hudson River between Rogers Island at Fort Edward (RM 194) and Lock #2 (RM 163.5). The low resolution coring sample locations (zones) in the TI Pool are shown in Plate 2-1 and summarized on Table 2-1. The locations were selected to represent a range of sediment types and sediment PCB inventories, with emphasis placed on areas of greatest PCB contamination. Fifteen small zones or clusters were selected within the TI Pool for a total of 60 low resolution core sites. In addition, four near-shore locations within the TI Pool were sampled during the low resolution coring program. Downstream from the TI Dam, seven previously identified *hot spots* in the Upper Hudson were sampled. The locations of the NYSDEC *hot spots* in the project area along with the associated low resolution coring locations are listed on Table 2-1 and shown on Plate 2-1. The number of cores taken in each of the *hot spots* was roughly proportional to its mass and spatial extent. To establish limits on the spatial extent of contamination at some of the larger *hot spots*, a few samples were placed beyond the original boundary defined by NYSDEC to examine the accuracy of the boundary. In addition to the cores associated with the *hot spots*, thirteen low resolution cores, roughly equivalent to the sampling intensity of one large *hot spot* (approximately 30 samples), were used as near shore/exploratory samples in four areas in which previous sampling was minimal or non-existent, and where bathymetric and/or sedimentological data suggested potential contamination.

Sample locations were surveyed at the time of collection using shoreline control points established prior to core collection. Estimated accuracy of all coring locations is ± 3 -feet. Within the TI Pool, field personnel attempted to re-occupy the NYSDEC locations. The original specification in the sampling plan stated a goal of ± 20 -feet about the NYSDEC location. In fact, the field team was much more successful, achieving a median distance of 3-feet between the 1984 and 1994 locations and only one 1994 location differed by 20-feet from the targeted 1984 location. Figure 2-1 shows the distribution of the distances between the 1994 locations and their targeted 1984 sites. Because of the success of the coring location control, 1984 to 1994 changes in total PCB inventory due to sample location differences were kept to a minimum.

2.2.2 Sample Preparation

The low resolution coring sampling plan (TAMS/Gradient, 1994) detailed a coring program to collect 39-inches (97.5-cm) of sediment at each coring location, conditions permitting. A core length of thirty-nine inches was selected based on the earlier NYSDEC studies which found PCB contamination principally in the top 24 inches of sediment. Twelve inches more were added to the goal to generously allow for additional deposition since the earlier surveys. Lastly, three inches more were added for a radionuclide sample to be collected below the main core segments. Since the main objective was not to simply collect a 39 inch core but rather to obtain all recent deposition, cores less than the prescribed goal were expected. Low resolution cores were obtained by a “vibra-coring” technique where a 4-inch (10-cm) diameter clear plastic tube was advanced through the sediment by applying pressure and vibration to the top of the tube. This served to partially liquefy the sediments along the walls of the tube and permit greater penetration of the tube into the river sediments. A sediment catcher or shoe was attached to the bottom of the coring tube to minimize the loss of sediment from the tube during retrieval. By comparison, the high resolution cores were collected in 2.5-inch (6.3-cm) diameter plastic tubes by applying pressure only. A check valve at the top of the core, rather than a shoe at the bottom, was used to prevent sediment loss during retrieval of the high resolution cores. Once obtained from the river, low resolution cores were then intended to be sliced into three 12-inch (30-cm) sections and one 3-inch (7.5-cm) section for subsequent analyses, when a full 39-inch core was obtained. Cores less than 39 inches were acceptable subject to field review by the field geologist. In essentially all cases, the coring apparatus was advanced until the equipment could not push it further. The core was then retrieved and the recovered material was examined by the field team. The average core length of 23 inches (57.5 cm) was substantially less than the goal of 39 inches (97.5 cm) and many core recoveries were less than 15 inches (37.5 cm). Generally, four segments were taken from cores 27 inches or more. As a result, the median segment thickness for the first three core layers was about 9 inches (22.5 cm), while still leaving a bottom 3-inch layer. For cores less than 20 inches, the field geologist evaluated the stratigraphy of the core and decided where to slice the core based on factors such as changes in color or grain size. Nonetheless, as will be discussed later, the evidence suggests that most cores were advanced through all potentially PCB-contaminated sediment.

Of the 170 cores collected for the program, 73 cores were sufficiently long so as to yield four segments per core. Fifty-five cores yielded three segments per core while 41 cores yielded

only two segments per core. One core (LR-02C) yielded only one segment. Besides two to four main core segments, in each instance the top portion of the top segment (0 to 1-inch) was used for ^7Be and ^{137}Cs radionuclide analyses and the bottom segment was used exclusively for ^{137}Cs radionuclide analysis. The overlying one to three main segments were analyzed for PCB and other analytes as discussed below. Core LR-02C was not analyzed for radionuclides. Table 2-2 provides a summary of the cores collected in terms of layer thickness and depth, the number of each core type collected (*e.g.*, number of two-layer cores), and the overall core lengths for each core type. Figure 2-2 is a summary diagram of the core segment thickness and depth. Figure 2-3 provides an illustration of how the cores were subdivided for analysis.

The actual slicing intervals for each low resolution core were selected by the field team based on visible sediment stratigraphy and analytical sample requirements as well as the prior NYSDEC core slicing intervals when applicable. Once the slicing intervals were selected, the core was extruded into pre-weighed stainless steel bowls for bulk density determination and homogenization. After homogenization, the sample was sub-sampled for various analytes as discussed below. During processing, samples were also field classified as clay, silt, fine-to-coarse sand, and gravel. The presence of minor quantities of other soil types, as well as organic materials and soil color, were also noted by the field geologist.

Sample nomenclature was similar to the high resolution coring program with one important difference. Core intervals were incorporated as inches and not centimeters, as was done previously. This was done to avoid lengthening the standard Phase 2 eleven-character identification (ID) string to account for samples greater than 40-inches (100-cm) in depth. The information encoded within the low resolution sample ID is as follows:

AA-00A-0000-A

where “A” represents a letter and “0” represents a number.

For the low resolution coring effort, the first letter was assigned an “L”. The second letter was assigned an “R” for samples collected from clusters within the TI Pool. For samples collected downstream of the TI Dam, the second letter was assigned an “H”. The next three characters represent the core location. The first two digits were assigned the number of the investigation zone in which the core was collected. The Thompson Island Pool locations were assigned numbers in the range of 01 to 19 corresponding to the cluster number. The Hudson River sample locations

below the TI Dam were assigned values corresponding to the two-digit *hot spot* number (*i.e.*, 25, 28, 31, 34, 35, 37, or 39). The alpha character which is the third character of this triad designates one of the three to 15 cores obtained from the cluster or *hot spot* area. Thus, “A” would represent the first core from the area, “B” the second, and so on. The last four digits of the ID represent the depth interval of the core segment in inches, with the first two digits corresponding to the top of the core segment and the last two digits corresponding to the bottom of the core segment. As was the case for previous efforts, the final letter is reserved for QC sample designations where applicable - D (Duplicate), and M (Matrix Spike or Matrix Spike Duplicate).

As an example, the sample designated LH-28K-0918 would be the low resolution core sample (LH) from *Hot Spot* 28. The “K” indicates the eleventh core in that *Hot Spot*, and 0918 indicates that the segment (section) was from the 9 to 18-inch (23 to 45-cm) depth interval.

2.3 Sample Analyses

Analytical parameters for the low resolution coring included:

- PCB congeners by capillary column gas chromatograph/electron capture detector (GC/ECD; with a limited number of confirmation analyses by GC/ion trap detector [ITD]);
- Radionuclide analysis;
- Total Organic Carbon;
- Total Kjeldahl Nitrogen;
- Grain-size distribution by sieve and laser particle analyzer (Laser);
- Grain-size distribution by sieve and hydrometer analysis (American Society for Testing and Materials [ASTM]);
- Percent solids; and
- Bulk density.

The analytical method for PCB congeners is provided in Appendix A. Non-PCB chemical and physical properties analytical methods are discussed in Appendix B.

As mentioned briefly in the previous sections, not all samples were analyzed for all parameters. This choice was based on the analysis type and intended use of the data. The typical sample set generated for each core was as follows:

- Radionuclide (beryllium-7 [^7Be] and cesium-137 [^{137}Cs]) analysis of sediment from a portion (half) of the 0 to 1-inch (0 to 2.5-cm) interval;
- PCB congeners from up to three layers of sediment, each about 9-inches thick;
- Laser grain-size distribution analysis of sediment from 0 to 9-inches;
- Bulk density for all sediment layers;
- Percent solids for all sediment layers greater than 1-inch; and
- Radionuclide (^{137}Cs only) analysis of sediment from a 3-inch layer immediately below the deepest layer analyzed for PCBs.

Roughly two-thirds of the cores had one to three additional grain-size distribution analysis by a standard ASTM sieve and hydrometer technique performed on one of the core intervals analyzed for PCBs. A subset of these samples was obtained from the top core slice permitting a direct comparison between the laser and ASTM techniques, discussed later in this report. A small subset of the core samples, roughly one in twenty, was analyzed for total organic carbon and total kjeldahl nitrogen. Figure 2-3 provides an illustration of how the cores were subdivided for analysis and Table 2-3 provides a tally of the number of analyses conducted for each analyte, excluding duplicates. As shown in Figure 2-3, only one half of the top 1-inch slice was used for radionuclide analysis. The other half of the slice was added to one half of the core portion from 1 to 9- inches and homogenized prior to subsampling for PCBs and other analytes.

Two additional analyses were slated to be collected or performed during the low resolution sediment coring program, including reduction/oxidation potential and total carbon/total nitrogen content. The results for reduction/oxidation potential were all rejected during the data quality review due to field calibration problems. Samples collected for total carbon/total nitrogen content were inadvertently held beyond acceptable sample holding times while finalizing a laboratory contract and were therefore never analyzed. The original low resolution sampling plan (TAMS/Gradient, 1994) also called for grain-size distribution analysis based on sieve and hydrometer to be performed for all samples. However, prior to beginning the field operation, this requirement was reduced to 150 samples, including duplicates.

Sample quality assurance followed the guidelines defined the Low Resolution Sediment Coring Sampling and Analysis/Quality Assurance Project Plan (TAMS/Gradient, 1994). Duplicate analyses were performed on field-generated sample splits at the rate of 1 in 20 samples. Data usability was reviewed for all analytes and is discussed in Appendix A. In general, data quality objectives were met with the exception of the reduction/oxidation measurements as discussed above.

2.3.1 PCB Congener Analysis

PCB congener analyses were performed on a rigorously homogenized core segment by a wet sediment soxhlet extraction followed by analysis on a dual capillary column gas chromatograph with electron capture detectors (GC/ECD). Roughly 10 percent of the sample analysis was confirmed via a second analytical technique, gas chromatography with an ion trap detector (GC/ITD). This confirmation was limited to samples with high PCB concentrations due to the higher (less sensitive) detection limits characteristic of this technique. These techniques are the standard congener-specific techniques used throughout the Phase 2 investigation. Use of these techniques guaranteed comparability of the low resolution coring results for PCBs with those obtained in the earlier Phase 2 studies. Due to improvements in the techniques achieved during the earlier Phase 2 studies, a total of 145 congeners was reported for each low resolution core PCB analysis, including 108 calibrated (target) congeners. However, to maintain comparability among the Phase 2 program, only the original 126 congeners including 90 targets are discussed and presented here. In general, the additional 19 congeners did not contribute substantively to the sediment PCB inventory, the main focus of this report. At the beginning of the Phase 2 investigation in 1992, standards only existed for 90 of the 209 PCB congeners. Retention times were known for an additional 36 congeners, bringing the total number of identifiable congeners to 126 at the initiation of the Phase 2 program. Subsequent to the start of the program, many more individual congener standards have been made available, thus enabling the increase to 145 identified congeners in the low resolution sediment core samples. As discussed in the DEIR (TAMS *et al.*, 1997), use of the original 126 congeners including the 90 calibrated congeners captures more than 90 percent of the original Aroclor 1242 and a higher percentage of the other Aroclors. Results for all 145 congeners analyzed in the low resolution cores are reported in the Phase 2 database (Release 3.5, June, 1997).

The congener-specific GC/ECD analysis performed for the low resolution coring does not rely on arbitrarily assigning Aroclor identification, but enables a total PCB concentration to be calculated, regardless of peak or congener composition. This is especially significant for congener mixtures which may have been subject to dechlorination, and no longer resembles the original Aroclor mixture. Since the major goal of this investigation was to examine the PCB inventory in a variety of sediments, this ability to calculate total PCB concentration is particularly important. However, in order to compare the congener-specific data to previously reported data, Aroclor data were calculated by summing the concentrations of the congeners present in each Aroclor mixture based on Aroclor standards analyzed via the Phase 2 congener-specific technique. In this manner the Phase 2 low resolution coring results can be compared with earlier studies which were based on Aroclor quantitation techniques.

2.3.2 Radionuclide Analysis

The radionuclide analytical procedure was restricted to the isotopes cesium-137 (^{137}Cs) and beryllium-7 (^7Be). ^7Be data were obtained and used to date the top of the core, and the ^{137}Cs data were used to verify that the core has penetrated all recent (*i.e.*, post-1954) sediments. Analysis of radionuclides in sediment cores provided a means of establishing the sediment core chronology. Studies of sediment cores in the Hudson have demonstrated the occurrence of well-documented radionuclide events which can be used to establish sediment accumulation rates at various locations throughout the Hudson. By determining the activities of ^{137}Cs and ^7Be , it is possible to verify that the core collected includes the depositional period from the time of core collection back to 1954.

^{137}Cs is a persistent (half-life of 30 years) anthropogenic radionuclide that has two distinct events associated with it. The first event corresponds to the onset of atmospheric atomic weapon tests in 1954, which is indicated in the sediments by the first appearance of ^{137}Cs . Background levels prior to 1954 are essentially zero for this radionuclide. Therefore, ^{137}Cs analysis of the bottom core segment verified for most cores that they extended at least as far back as 1954. A non-zero result for ^{137}Cs indicated that the core collected did not include sediment deposition prior to 1954. Previous data have indicated that PCB deposition in the Hudson River prior to 1954 is not significant in comparison to PCB discharges since then (TAMS *et al.*, 1997).

^7Be is a short lived (half-life of 53.6 days), naturally-occurring isotope whose presence in the sediments indicates recent deposition or interaction with surface waters within the six months prior to sample collection. Approximately 90 percent of the ^7Be activity dissipates within 180 days. Thus, this radionuclide was used to initially test a core top (0 to 1-inch) for the presence of recently deposited sediment. Absence of ^7Be is attributed to a core collected in a non-depositional area or an area experiencing scour (erosion) of river sediment.

2.3.3 Total Organic Carbon and Total Kjeldahl Nitrogen

Total organic carbon and total kjeldahl nitrogen analyses (TOC/TKN) were performed on about seven percent of the samples analyzed for PCBs, representing about 15 percent of the coring sites. These analyses were performed on individual core segments randomly selected from the various cores. Specifically, one sediment segment was analyzed per core in 26 cores with nine surface segments, seven second layer segments, and 10 third layer segments analyzed. TOC analyses were accomplished by the USEPA Region II method involving the direct combustion of the sample. (TAMS/Gradient, 1994). TKN analyses were accomplished by a modified version of USEPA method 351.2 (TAMS/Gradient, 1994). TOC and TKN analyses were performed on the same subset of samples so as to permit the calculation of a molar carbon-to-nitrogen ratio. These analyses were originally intended solely to supplement the planned total carbon/total nitrogen (TC/TN) analyses which were to be run on every core sample. This approach was the same as that used for the high resolution cores. The TOC/TKN analyses were intended to confirm that the TC/TN results closely matched the organic C/N results. However, due to exceedances of holding time, none of the TC/TN analyses were run. As a result, only the randomly selected TOC/TKN samples were available to characterize organic carbon and nitrogen levels in the low resolution coring program study areas.

2.3.4 Physical Properties

Grain-Size Analysis

Grain-size analysis was performed on a large subset of the low resolution sediment core slices (except the bottom segment which is analyzed for ^{137}Cs only). In the top core segment only, grain size distribution was determined by mathematically combining results from an ASTM sieve

method and a laser-particle analyzer method (Phase 2B SAP/QAPjP Appendix B-5). The smaller particle (less than 2-mm) grain-size distribution was determined by the laser particle analyzer-based methodology. Larger particle size fractions (greater than 1-mm) were determined by the ASTM methods. There was an overlap between the methods in the 1 to 2 mm-range, thus providing a means of correlating and cross-checking data between the two methods. The principal purpose for these samples was to further support the grain-size distribution and side-scan sonar analysis presented in the previous Phase 2 report (TAMS *et al.*, 1997). An additional set of sediment samples was analyzed using ASTM Methods D421-85 and D422-63 including hydrometer analysis. These samples will be used to characterize the sediments for engineering analyses.

Bulk Density

Review of the method for deriving bulk density used in the previous studies indicated that the method was somewhat crude and may not be representative of *in situ* density. Although the data review in general indicated that the average bulk density values from the NYSDEC studies were reasonable, the data for some individual points were not (TAMS *et al.*, 1997). Therefore, to address concerns regarding the accuracy of previously-derived bulk sediment densities, new data for this property was obtained during the low resolution coring program.

Bulk density was measured in the field by extruding a known volume from the core tube into a pre-weighed stainless steel bowl and then re-weighing the bowl. Bulk density was calculated simply as the ratio of the mass weighed to the known volume. The results were used to calculate the total PCB inventory. Reported bulk density values were restricted to a range of 1 to 3 g/cc. Values outside this range were rejected.

Percent Solids

Percent solids were determined for all samples analyzed for PCBs as well as the bottom slice analyzed for ¹³⁷Cs. This method involved the simple weighing of a sample portion before and after drying. The original results were reported as percent moisture. These values were converted to percent solids by simply subtracting the percent moisture value from 100 percent. The percent solids data were combined with the bulk density data to calculate the solids specific weight (the weight of solids per unit volume of sediment) and the solids density (the mass of solids per unit

volume of solids). Typically, the solids density should be in the range of 2 to 2.5 gm/cc. Sample values for solid bulk densities outside the range of 1 to 3 gm/cc were excluded from further analysis. This exclusion incorporated the bulk density, percent solid values, solids specific weight and the solids density. That is, unless the bulk density and percent solids yielded internally consistent results, all four values (two measured, two calculated) were excluded from further analysis.

2.4 Summary of Analytical Results

This section presents a brief general description of the analytical results obtained for the low resolution coring program. The interpretation of the results is presented in Chapters 3 and 4 of this report.

2.4.1 PCB Congener Analysis

PCBs were detected in every sample analyzed for PCBs. The range of total PCB concentrations (<0.05 to 1,352 ppm) was slightly less than the range obtained for the high resolution cores (<0.05 to 2,500 ppm). Nonetheless, these values represent substantive PCB inventories, especially when the segment thickness is considered. The low resolution sediment values represent a 9-inch median thickness, as opposed to the 0.8 to 1.6-inch high resolution core layers. Thus, the high values obtained in cores from the Upper Hudson do not appear very unusual, given their occurrence in both the low resolution and high resolution programs.

A summary of the results from the cores is presented on an area basis and a depth basis in Table 2-3. The arithmetic mean and median concentrations in the TI Pool are comparable to the areas downstream of the TI Pool. Mean sediment concentrations obtained from the low resolution core results should not be directly compared between the two regions because the 76 cores analyzed in the TI Pool and 94 cores taken downstream of the TI Pool were intended to characterize local conditions in several areas and do not comprise a spatial coverage sufficient to calculate PCB inventories for these areas directly. Histograms of the total PCB concentrations in all core segments and only in shallow (top) core segments are shown in Figure 2-4. The total PCB concentrations are statistically skewed, with an approximately normal distribution when data are

log normalized. The log-normal nature of the shallow segment data was confirmed by a W test for normality, although the entire log-transformed data set (*i.e.*, all core segments) did not pass the W test for normality. The lack of normality is largely the result of the inclusion of very low PCB concentrations, typically found in deep core segments. In many of the subsequent analyses, these samples (total PCBs < 100 µg/kg) are excluded due to quantitation issues, thus making the remaining data set more log-normal. The majority of statistical calculations dealing with PCB concentrations included in this report are based on the log-transformed data.

The core results presented by depth show an important finding. PCB maxima are principally found in the top-most core layer (61 percent or 104 out of 170 cores), representing shallow sediments (median depth of 9-inches). These results indicate that burial of PCB-bearing sediments is not occurring on an extensive basis and that high concentrations of PCBs remain relatively close to the sediment/water interface. The assignment of the sediment PCB maximum to a given layer is based on several criteria including:

- Occurrence of the maximum PCB concentration for the core in that layer; and either
- Occurrence of a deeper layer with lower PCB levels; or
- Absence of ¹³⁷Cs in the radionuclide layer at the bottom of the core when the maximum PCB layer is immediately above.

These criteria are based on the known PCB deposition history for the Upper Hudson as recorded in sediment cores (Bopp and Simpson, 1989; TAMS, *et al.*, 1997). In particular it assumes there is only one PCB maximum and that ¹³⁷Cs presence indicates PCB presence. Thus, when a core has an assigned PCB maximum, it is inferred that the maximum concentration in the sediments at that location has been captured by the core, and that the core represents the majority of the PCB inventory. When ¹³⁷Cs is not detected in the core bottom, the core is assumed to represent the entire PCB inventory. On ¹³⁷Cs alone, 119 cores are assumed to represent complete inventories. By utilizing the criteria given above, an additional 15 cores can be added to this category, bringing the percentage of complete (and nearly complete) cores to 134 or 79 percent of the cores collected.

In a portion of the cores collected (36), these criteria were not met and the core PCB maximum was unassigned. In these instances, the possibility that the PCB maximum

concentration lies below the bottom of the core cannot be ruled out. Thus, these cores are listed as having an unknown maximum. It should be noted that the majority of these unknown maximum cores (22 of 36) represent short (<15 inches) 2-layer cores where additional sediment could not be obtained. Given the inability to further advance the collection apparatus, it is unlikely that these areas are underlain by large amounts of high PCB-bearing sediments, typically silts and fine sands which are easily cored. Also, as noted above, the PCB maxima are generally found in the shallowest sediments. Thus, even though these cores are incomplete, it is unlikely that the PCB inventories are much greater than calculated.

For the multiple layer cores with unknown PCB maxima, the depth of penetration is similar to many of the complete cores. The results from the complete multiple layer cores indicate that the majority of PCB contamination resides in the two uppermost layers (top 9 to 18-inches). This would suggest that the incomplete multiple layer cores are likely to capture the majority of the sediment PCB inventory since they typically extend below 18 inches. However, this is much less certain than for the incomplete 2 layer cores. In particular, these incomplete multiple layer cores were more commonly found below the TI Dam and have important implications for the sediment mass estimates from this area. Further interpretation of these cores is presented in Chapter 4 during the discussion of the *hot spots* below the TI Dam.

The fact that the PCB maxima are found largely in the shallow sediments provides useful information for the cores labeled incomplete, as noted above. This implies that for most of these cores, the material retrieved probably represents the majority of the PCB inventory at the coring site. PCB estimates derived from these incomplete cores probably underestimate the actual sediment inventory in the affected cores by less than 50 percent. Discussions of sediment-PCB inventories and their comparison to earlier surveys are presented in subsequent chapters of this report.

The total PCB values discussed above were based on congener-specific analysis, just as all Phase 2 results have been. Although the 145 congeners were reported for the low resolution core samples, the total PCB results as well as the congener-specific discussions to follow are based on the original 126 congeners to maintain consistency in the Phase 2 discussion. Exclusion of the 19 additional congeners has little effect on estimates of sediment PCB mass since these congeners represent less than 1.5 percent of the total PCB concentration, on average. In all but five of the 371

PCB analyses, these 19 congeners represented less than six percent of total PCB mass. For the five samples where these 19 congeners were greater than six percent, the total PCB concentration was less than 32 µg/kg (0.032 ppm). Thus, these congeners do not represent substantive PCB mass and are ignored in subsequent discussions in this report. Some of these congeners may be used in PCB pattern comparisons as part of the ecological assessment.

Sample splits were generated in the field and run as blind duplicates by the laboratory. A total of 23 split pairs was generated. The fields were compared using a relative percent difference (RPD) calculated as follows:

$$RPD = \left| \frac{R_1 - R_2}{(R_1 + R_2) / 2} \right| * 100\%$$

where:

R_1 = result for original sample
 R_2 = result for duplicate sample

An RPD of zero is ideal, meaning the paired measurements are identical. An RPD of 50 percent represents a difference of 40 percent between the smaller and larger measurement based on the larger measurement. For example, a pair of measurements of 6 and 10 would have an RPD of 50 percent. Figure 2-4 shows the level of precision attained for field replicates. The average RPD was 36 percent, and the median RPD was 27 percent. These results suggest that, on average, measured results would be expected to fall within ± 36 percent of the true PCB concentration for the sample.

Field duplicate sample pairs were also examined for the reproducibility of the congener patterns by performing a simple regression on the normalized congener values. Congeners were normalized to BZ #52, as was done in previous Phase 2 work. An ideal match between the sample pairs would yield a regression slope of unity (1) and a regression coefficient (R^2) of unity. Figure 2-5 shows these example regressions run on field split pairs. The close agreement between the field split congener ratios is evident by the low level of scatter in each diagram. Figure 2-6 provides a histogram of the regression slopes for the field pairs. The zero intercepts for all of these regression pairs fell within a few percent of zero (Figure 2-5), largely dictated by the large number

of non-detect results. Thus the slope of these regressions is the indicator of agreement. Note that the slopes for two-thirds of the replicate pairs fall within 10 percent of unity, indicating close agreement of the congener patterns. Also notable are the two outliers. The most distant of the two outliers is the result of detection limit differences between the replicate pairs. One sample was roughly four times more concentrated. This led to several congeners being detected in one sample while not being detected (effectively zero) in the other, which yielded the poor slope. When the non-detect/detect pairs were excluded, the remaining results yielded a slope close to unity. The second outlier was characterized as having a few congeners whose ratios were very disparate while the remaining congeners agreed well. This was typical of all of the poorer fits only to a lesser degree, indicating that in general, most congener ratios were reproducible to within a few percent. In general, agreement between congener patterns in replicate pairs was substantially better than the ability to reproduce absolute mass. This suggests that sediment heterogeneity in concentration as well as the ability to completely homogenize sediment samples will probably be the main source of analytical uncertainty for PCB results.

2.4.2 Radionuclide Analysis

The sampling program was roughly split in half between the TI Pool and the areas below the TI Dam. Seventy-six cores were collected from the TI Pool and 94 from the area below the TI Dam, yielding 170 cores in all. Each of these cores were analyzed for radionuclides in the top-most and bottom-most layers (Table 2-3). It is important to note here how radionuclides were used in the interpretation of the low resolution coring data. Specifically, radionuclides were examined primarily on an absence/presence basis. The radionuclide ^{137}Cs was first introduced to the Hudson (and most watersheds in the Northern Hemisphere) in 1954 as atmospheric fallout with onset of atmospheric weapons testing by the US. As a result of the retention of ^{137}Cs in the soils of the watershed and subsequent erosion of these soils, all post 1954 sediments in the Hudson have readily measurable levels of ^{137}Cs . The introduction of PCBs into the Hudson potentially predates ^{137}Cs by a few years since PCB manufacturing at the GE facilities began prior to the appearance of ^{137}Cs . However, as was shown in the analysis of the high resolution cores (TAMS *et al.*, 1997), little if any detectable levels of PCBs are present below the first appearance of ^{137}Cs in a core. This is illustrated in the core profiles shown in Figure 2-7. On this basis it is evident that if ^{137}Cs is present in a Hudson River sample collected below Hudson Falls, the sample must contain PCBs. Similarly, if ^{137}Cs is not detected in a sample, it is likely to contain little or no PCBs. When ^{137}Cs

was not detected in a core bottom, the core was considered to be “complete” (*i.e.*, it represents all recent [post-1954] deposition and all substantive PCB deposition). If ^{137}Cs was present in the bottom layer, the core did not capture the entire PCB inventory and was labeled “incomplete”. In these instances, nearby cores may be applied to estimating what was missed. In any case, the magnitude of the ^{137}Cs level in the sediment was principally interpreted internally to the core since the concentration could be affected by several factors including the fine-grain content of the core, the mixing of ^{137}Cs -bearing and non-bearing sediments within the segment, and the actual sediment age which make core-to-core comparisons less certain.

Similarly, the ^7Be results were considered on an absence / presence basis. Presence of ^7Be indicated very recent (six months or less) deposition at the coring site. Absence of ^7Be indicated a non-depositional site at a minimum, as well as the potential for sediment scour.

^{137}Cs was not detected in the bottom layer of the 120 of the 170 cores collected. These 120 cores, representing 70 percent of the coring effort, were considered *complete*. This indicates that the PCB contamination contained in these 120 cores is representative of the entire current PCB inventory at these sites; *i.e.*, no substantive PCB contamination exists below the depth of core penetration. In looking at the cores above and below the TI Dam, the success rate for *complete* cores was greater above the TI Dam than below it. Sixty-one cores from the TI Pool (roughly 81 percent) included all recent deposition as demarcated by ^{137}Cs . Conversely below the TI Dam, the rate for successful core collection was only 60 percent, with ^{137}Cs detected in 36 of 94 cores. The ^{137}Cs and ^7Be results for one core in the TI Pool were lost and so this core is excluded from the above tallies.

The reason for the difference in success between the TI Pool and areas downstream is unknown, but is at least partially due to differences in sampling approaches. Within the TI Pool, sites were preferentially selected where previous NYSDEC coring work was successful. In addition, sites were selected in relatively homogeneous areas based on both sediment and PCB criteria. In the study areas below the TI Dam, sampling locations were selected to demarcate *hot spots*. This included placement of some cores in areas beyond *hot spot* boundaries where recoveries were less certain.

The length of the ^{137}Cs -bearing cores was consistently less than those considered *complete*, about 5 to 7-inches shorter based on the median core length. This suggests that the ^{137}Cs -bearing cores were collected in areas more difficult to penetrate, perhaps due to sediment type, or due to underlying harder substrate, relative to the successful core sites. A comparison of *complete* and *incomplete* cores above and below the TI Dam based on core lengths, layer thickness, and the sediment types associated with each layer is provided in Table 2-4. Median overall core lengths for *complete* cores are relatively comparable, but in both instances the *incomplete* cores are distinctly shorter than the *complete* cores. It was originally thought that this distinction might result from coarser sediment types for the *incomplete* cores, making core collection more difficult. However, as can be seen in Table 2-4, the proportions of silt, fine-sand, and coarse-sand samples in the complete and incomplete core sets are quite similar. This suggests that core sediment type does not affect the ability to collect a *complete* core. From this conclusion, it may be inferred that other causes, such as a change in the underlying substrate, may be responsible for the collection of *incomplete* cores. Other potential causes include loss of the core bottom during retrieval. It is important to remember here, however, that the majority of cores (70 percent) were *complete*. Based on the PCB data discussed below, it is likely that an additional 15 cores may be considered nearly *complete*, bringing the fraction of successful cores to 79 percent.

The ^7Be results for surface sediments for each core were used to establish the current deposition condition at each site. Of the 169 cores analyzed for ^7Be , 119 cores indicated the presence of ^7Be and, therefore, recent deposition. However, this was not proof of a continuous depositional site but only deposition within the last six months. This issue is discussed in subsequent chapters of the report when 1984 and 1994 sediment inventories are compared. It should also be noted that 50 cores, or more than 30 percent of the core sites, had no ^7Be , indicating that the site was currently non-depositional and potentially undergoing scour.

All coring sites contained ^{137}Cs in the surface layer, indicating that some PCB-contaminated sediment had accumulated between 1954 and 1994.

2.4.3 Total Organic Carbon and Total Kjeldahl Nitrogen

Total organic carbon and total kjeldahl nitrogen (TOC/TKN) analyses were originally intended to confirm the scheduled total carbon and total nitrogen (TC/TN) analyses, respectively.

The latter two analyses measure all carbon and all nitrogen while the former analyses measure just the organic forms. Based on the high resolution sediment cores results, it had been shown that TC/TN and TOC/TKN yield similar values for Hudson sediment samples, indicating that most sediment carbon and nitrogen were in organic forms. Nonetheless, the results of the TC/TN and TOC/TKN from the Low resolution Sediment Coring Program were intended to provide further confirmation of this finding.

Lacking the TC/TN results, the TOC/TKN results are still useful as measures of sediment properties. The mean and median TOC values were five and six percent of sediment mass on a dry weight basis with a range of 0.2 to 11 percent (Table 2-3), which is quite comparable to the high resolution sediment cores. The results are also typical for organic-rich, fine-grained sediment.

The TKN results for the sediments had similar values for mean and median at 1,640 and 1,370 ppm, respectively (Table 2-3). The range in TKN was similar in scale to that for TOC, as might be expected since both measures are tied to organic matter.

The molar ratio of carbon to nitrogen is sometimes used as an indicator of the source of the organic material in the sediment. Specifically high ratios (>80) are indicative of a wood cellulose source while low values (about 10) are typical of soil carbon and algal production (Söderlund and Svensson, 1976). Values in between would be expected in blends of wood cellulose and soil or algal-based organic materials. Wood cellulose would not normally be an important carbon source in a river system. However, in the Hudson, because of its history as a wood processing area, wood cellulose is much more common. In addition, it has been reported in the literature (*e.g.*, Bopp and Simpson, 1989) that wood chip-bearing sediments tend to contain enhanced levels of PCBs relative to other sediments. Thus the C/N ratio may serve as a flag for these layers. The C/N ratio in the limited low resolution coring data set varied over a range of 11 to 82, with a median ratio of 40 (Table 2-3). The results indicate the presence of some woody material in the organic matter contained in many of the samples since a value around 10 would be expected in the absence of wood cellulose. This confirms the visual classification which notes wood chips in 19 of the 27 samples run for TOC and TKN. Unfortunately, no correlation was seen between the visual presence of wood chips and the C/N ratio. The range and mean C/N ratio for the 19 samples with wood chips noted was not statistically different from the range and mean ratio for the seven samples where wood chips were not noted. This may be the result of the small samples size (26

samples), or of the difficulty in homogenizing wood chips in the sediment sample. Given the median C/N value of 40, which is well above the expected value of 10 for soil and algal-based organic matter, these results suggest that wood chips or woody material are present as part of the organic matter throughout much of the Upper Hudson sediments.

2.4.4 Physical Properties

Grain-Size Distribution

Low resolution sediments were classified by three separate techniques, specifically:

- visual field inspection;
- combined sieve and laser particle analysis (Laser); and
- combined sieve and hydrometer analysis (ASTM).

Results from these techniques are summarized in Tables 2-3 and 2-4. Both Laser and ASTM techniques were applied to a large subset of the samples collected. Visual field inspections were performed for every sediment sample. Samples are represented in Table 2-3 based on the largest grain-size fraction. It should not be inferred from this table that any sample is 100 percent silt, fine- sand, etc. In fact, most sediment samples were considered to be poorly sorted with a significant fraction (>10 percent) of other sediment types. In many instances the largest fraction represented less than 50 percent of the sample.

Evident in all three data sets is the predominance of samples classified as silt (fines in the case of the ASTM results). The predominance of this fraction reflects the orientation of the sampling program, *i.e.*, to obtain cores from areas of substantive PCB contamination, generally areas of fine-grained sediments. In general, the three methods yield similar results for most samples. The results of these methods are compared by principal fraction in Figures 2-8 to 2-10.

In Figure 2-8 the results of the visual and Laser classifications are compared for the shallow sediments only, (*i.e.*, just the top slice of each of 169 cores). The uppermost diagram shows the coincidence between principle fraction by visual inspection versus that obtained by the Laser technique. The two lower diagrams represent the distribution of matched samples as classified by

each method. In most instances, the two methods agree on the principal fraction for samples classified as silt and fine-sand, effectively verifying the subjective visual classification. When the two methods disagree, it is usually by only one class (*i.e.*, fine-sand by visual inspection is assigned silt by the Laser technique). In most of these instances, the actual fractions are very close (*e.g.*, 35 percent silt and 32 percent fine-sand). The coarser materials, *i.e.*, medium- or coarse-sand and gravel, were not as constant as silt and fine-sand for the two methods. In particular, the medium-sand as classified by visual inspection could be found in every class by the Laser method. This is indicative of the poor sorting of the coarse sediments, which made visual classification more difficult.

In Figure 2-9, the visual inspection results are compared with the ASTM method for samples (n=143) from a range of depths and locations, as opposed to the shallow sediment samples presented in Figure 2-8. Again, the two methods generally agree for silt and fine-sand; however, the coarser fractions are more problematic. As discussed above, this is attributed to the poorly sorted nature of the sample materials.

Figure 2-10 compares the results for the Laser and ASTM methods directly for the 69 shallow sediment samples run by both methods. The top diagram shows the agreement of the principal fractions between the two methods. Although the methods agree for most fines, the Laser method characterizes more samples as silt than does the ASTM method. This trend is apparent for all sediment classes, with the Laser method tending to characterize more samples into smaller fractions than the ASTM method. The lower half of Figure 2-10 is a histogram of the percent similarity calculated for each Laser-ASTM measurement pair. Percent similarity is calculated by summing the smallest value in each of the sediment classes for a pair of measurements as shown below:

	Sediment and Class Fraction					
	Silt	Fine Sand	Medium Sand	Coarse Sand	Gravel	
Laser Analysis of Sample 1	45	28	12	15	0	= 100%
ASTM Analysis of Sample 1	35	32	18	12	3	= 100%
	35	28	12	12	0	= 87% Similarity

The range of percent similarity for this data set is 34 to 98 percent with a mean value of 76 percent. This is quite similar to the work of Shillabeer, *et al.*, 1992, where a set of 406 sediment sample pairs was analyzed by both Laser and sieve techniques. A mean percent similarity of 79 and a range of 55 to 97 percent was obtained, with the Laser technique consistently predicting larger fractions of the finer sediments. This matches the results obtained for the low resolution coring program quite well. The authors attributed the difference to the way the techniques measure particles. Essentially the Laser technique reports the particle-size distribution by volume while the ASTM (sieve) method is sensitive to particle diameter and shape.

Thus, the two methods report different distributions for the same sample. Since the primary goal of these analyses was to classify sediments in a qualitative sense for potential PCB contamination, this difference is unlikely to be important. In particular, the Laser results can be applied directly to the existing Phase 2 database, to expand and confirm the correlations seen between the side-scan sonar and the confirmatory samples (TAMS *et al.*, 1997). This application is presented later in this report.

3. INTERPRETATION OF LOW RESOLUTION SEDIMENT CORING RESULTS

This chapter presents evidence to show how the low resolution coring results build on the previously collected Phase 2 data. Specifically, the PCB results of the low resolution coring program are compared and contrasted with the high resolution core (dated sediment core) results. Correlations among the various low resolution core analyses are also examined. Finally, the low resolution core results are interpreted along with the side-scan sonar data. As noted in Section 2.4.1, PCB concentration data from the low resolution coring program are log-normally distributed. For this reason, most graphical presentations in this chapter utilize a log-scale total PCB axis when displaying these results. Median and geometric mean values are good measures for the central tendency of log-normal data and will be used extensively throughout these discussions. Use of the median and geometric mean to characterize the log-normally distributed PCB data permits the use of various statistical tests to examine nature of the PCB data and its correlation with various ancillary parameters such as total organic carbon and bulk density. A summary of parameters obtained in the low resolution sampling program is provided in Table 3-1. It should be noted, however, that the geometric mean is not an appropriate value for the calculation of sediment mass. In this instance, the arithmetic mean is required. Characterization of sediment mass is examined in detail in Chapter 4 of this report.

3.1 Comparison between the PCB Results for the Low Resolution Cores and the High Resolution Cores

The High Resolution Sediment Coring Program obtained cores from fine-grained sediments from throughout the Hudson. As part of the interpretation of these results (TAMS *et al.*, 1997), several important correlations concerning anaerobic dechlorination were found, including the following:

- 1. All sediment PCB dechlorination losses could be explained by loss of the outer chlorine atoms (meta and para positions) from the PCB molecule.** No evidence for the loss of the inner chlorine atom (ortho position) or destruction of the PCB molecular structure was found. In support of this, it was shown that the molecular weight of a sample decreased in direct proportion to increases in the molar ratio of the sum of

five congeners, BZ# 1, 4, 8, 10, and 19, to that of the entire sample. This relationship would only hold if dechlorination was strictly limited to outer chlorines and if other possible destructive processes were minor.

2. **PCB mass loss by dechlorination was limited to 26 percent of the original deposited mass and that few samples ever approached this limit.** In fact, the mean mass loss was less than 10 percent assuming Aroclor 1242 as the original mixture.
3. **The degree of dechlorination increased with the logarithm of the total PCB concentration.** Thus, samples with PCB concentrations greater than 30 ppm exhibited various levels of dechlorination, while samples with concentrations of less than 30 ppm were relatively unaltered. This conclusion was perhaps the most important of the three.

One of the concerns with the high resolution sediment coring program was the issue of representativeness for other Hudson sediments. Since the high resolution sediment cores were obtained from select, high-deposition rate, fine-grained sediment environments, would they be representative of conditions throughout the Hudson where deposition conditions were not as favorable? The low resolution coring program was intended to generate a data set of spatially representative samples from a number of areas of the Upper Hudson. This data set was used to reexamine the relationships derived from the high resolution sediment cores.

As the first step in the re-examination, the change in the samples' molecular weight relative to Aroclor 1242 (MW) and the molar dechlorination product ratio (MDPR) were calculated for the entire low resolution coring data set. These terms are calculated as follows:

$$\Delta MW = \frac{MW_{A1242} - MW_{Sample}}{MW_{A1242}} \quad (3-1)$$

where: MW is the fractional difference in the mean molecular weight relative to Aroclor 1242;

MW_{A1242} is the mass-weighted mean molecular weight of Aroclor 1242; and

MW_{Sample} is the mass-weighted mean molecular weight of the sample calculated by:

$$MW_{Sample} = \frac{C_{Total}}{\sum_{i=1}^{10} \left[\frac{I}{mw_i} * \sum_{j=1}^{n_i} C_j \right]} \quad (3-2)$$

where: I is the homologue group number from 1 to 10;

mw_i is the molecular weight of homologue group I in g/mole;

n_i is the number of measured congeners in homologue group I ;

C_j is the concentration of congener j in $\mu\text{g/kg}$; and

C_{total} is the total concentration in the sample in $\mu\text{g/kg}$.

$$MDPR = \frac{\sum_{i=1,4,8,10,19} [BZ\#i]}{126} \quad (3-3)$$

$$\sum_{j=1} [BZ\#j]$$

where: $[BZ\#I]$ and $[BZ\#j]$ are the molar concentrations of congeners I and j , respectively in the sample (mole/kg); and 126 is the number of congeners for which consistent reliable identification and quantitative data were generated in the Phase 2 analytical program.

The term MW equals zero for Aroclor 1242, reported to be the main PCB mixture released to the Hudson (Brown *et al.*, 1984). The MW is positive for a decrease in molecular weight in the sample. If a sample is limited to dechlorination by loss of outer chlorines, the maximum value for MW is 0.223, corresponding to a mass loss of 26 percent. MW can have negative values if heavier Aroclor mixtures are present or if lighter congeners are lost from the mixture.

The MDPR equals 0.14 for a fresh Aroclor 1242 mixture. The maximum value is unity, assuming complete conversion of a mixture to BZ# 1, 4, 8, 10, 19 via dechlorination. The MDPR can never be negative by definition, since it is the ratio of two sums.

These terms were calculated for all low resolution sediment core samples with a total PCB concentration greater than 100 µg/kg. The concentration of 100 µg/kg was selected as a lower bound to avoid quantitation uncertainties associated with the lighter congeners that can occur at low concentrations. Table 3-2 provides a summary of the range, median and mean values for MW, MDPR, total PCBs, and an estimated mass loss based on the MW value. Immediately evident from the table is the consistency of the maximum level of dechlorination with the high resolution core results (*i.e.*, no sample attains the theoretical limit values for MW of 0.223 or for MDPR of 1.0, and few samples even get close). The average level of dechlorination as measured by MW is 0.1, corresponding to a mass loss of 12 percent. Considering that the low resolution coring sites were focused on the *hot spots* of the Upper Hudson, this result is very consistent with the DEIR conclusion that the average level of dechlorination throughout the freshwater Hudson is less than 10 percent.

It should be noted that the degree of dechlorination observed (MW = 0.10) for the median sediment concentration of 19 mg/kg is noticeably higher than would be expected from the results reported in the DEIR. Based on the high resolution core analyses, a sediment concentration of 19 mg/kg would have an expected dechlorination level MW of only 0.05, corresponding to a six percent mass loss. The reasons for the difference between the observed and expected dechlorination levels are discussed at length later in this chapter, as part of the analysis of MW, MDPR, and total PCB concentration.

Before exploring the relationship between MW, MDPR, and total PCBs (log transformed length-averaged) for the low resolution cores, it is first important to examine the relationship between MW and MDPR for these cores. This relationship is shown in Figure 3-1, which presents the regression line determined by the low resolution coring results, as well as the high resolution core regression line and the theoretical relationship. There is a close, but not exact, reproduction of the high resolution core regression by low resolution core data for MW versus MDPR. Although the difference between the two regression curves is minor, a test for significance using Chow's F test (Fisher, 1970) shows the coefficients of the two curves to be statistically different. A second statistical test, Theil's U statistic, indicated that the difference was minor, and likely due to differences in variance between the high resolution core and low resolution core results. Based on these statistical tests, both curves are sufficiently close to the theoretical relationship that they serve to support the original premise, *i.e.*, that dechlorination is limited to outer chlorines (meta- and para-

dechlorination) and that little, if any, in situ destruction of PCB molecules is occurring. Definitions for Chow's F test and Theil's U statistic can be found in the glossary as well as in the references (Fisher, 1970 and Theil, 1996).

The plot of MW versus MDPR confirms the first two high resolution core conclusions discussed earlier. Confirmation of the last conclusion from the high resolution cores that the degree of dechlorination increases with the total PCB concentration by the low resolution core results was more problematic. As part of the analysis, the low resolution core results were plotted as MDPR and MW vs total PCB concentration in the same way as the high resolution cores. Figure 3-2 presents the results for the low resolution cores as well as the regression line and confidence limits for the high resolution cores. Note that the confidence limits represent the 95 percent confidence limit of the individual data points and not the regression line itself. There is a distinct left shift in the low resolution core results relative to the high resolution core results and greatly increased data scatter.

Figure 3-2 also shows the layering information for the low resolution cores, with separate symbols for the top, second and third slices. With this information displayed, it is apparent that the majority of the scatter away from the high resolution core regression line stems from the deepest slices. The separation of these points becomes even clearer when the presence of ^{137}Cs in the bottom-most layer is considered. Deep layers from cores considered *complete* (no ^{137}Cs in the bottom layer) are almost exclusively responsible for the scatter away from the high resolution core regression line and confidence limits, as shown in Figure 3-3.

Although this was an interesting correlation, the underlying reason for this was less clear. The basic issue with these samples was their extensive degree of dechlorination given their very low sediment PCB concentration. In addition, these points were unique to those cores where the maximum PCB concentration was usually in the surface layer and where no ^{137}Cs was detected at depth. Cores with deeper PCB maxima and ^{137}Cs present generally fell within the high resolution core regression and confidence limit domain. When congener patterns of the deeper layers were compared with those from the top layers, it was found that in many instances, the deeper layer pattern closely matched that of the surface layer. The results for the selected core samples are very similar to those of all core segments, as illustrated in Figure 3-4 which shows three examples of the match between the surface and deeper layers. In each of the diagrams, a perfect match would have both a slope and R^2 of unity

(one). The values obtained are somewhat poorer than the values obtained for field split analyses, as discussed in Section 2.3.2. However, when they are compared to other top and deeper segment pairs which fall close to the high resolution core regression, the slope and R^2 are distinctly higher for the cores with no ^{137}Cs present at depth. (See Figures 3-4 and 3-5).

Given the strength of the trend observed for high resolution cores and that the low resolution cores generally followed or paralleled this trend when deeper layers from *complete* cores were excluded, it seemed clear that the scattered points must result from a different cause and that the relationship of increasing dechlorination with increasing PCB concentration was valid for results from both coring programs. The simplest and most likely explanation of the widely scattered points given the absence of ^{137}Cs in the bottom-most layer is cross-contamination of deeper sediments by overlying ones. Cross-contamination is of greatest concern when layers originally differed by several orders of magnitude. Incorporation of as little as a few tenths of a percent of overlying material would serve to create samples with low PCB concentrations that exhibited much higher degrees of dechlorination. The level of dechlorination in the PCBs in the deeper layer would be expected to match that of the more contaminated upper layers since any cross-contamination process would largely serve to dilute the mixture and not cause any change in the congener ratios. The terms MW and MDPR represent various PCB congener ratios and thus would also be unaffected by dilution.

The sensitivity of the results to cross-contamination stems in part from the way ^{137}Cs and PCBs are handled. ^{137}Cs measurements are performed directly on samples without any concentration or dilution steps. This technique is sufficient to discern recent deposition from pre-1954 sediment. Cross-contamination is not an issue since ^{137}Cs levels are generally measured over only a range of one to two orders of magnitude. Thus, a minor cross-contamination event (one percent of overlying material mixed into a deeper layer) will not be detected and a pre-1954 sediment will be correctly identified. On the other hand, PCB measurements are reported over nearly five orders of magnitude via laboratory dilution of sample concentrations. Thus a deeper sediment layer incorporating 0.1 percent by mass of an overlying layer at 500 mg/kg (ppm) yields a layer at 0.5 mg/kg (ppm), well within the range of PCB measurements. This layer would exhibit MW and MDPR values commensurate with the level of dechlorination expected for a 500 mg/kg (ppm) sample and not a 0.5 mg/kg (ppm) sample.

The potential to cross-contaminate low resolution samples relative to high resolution samples stems from the way in which cores were collected and processed. As mentioned in Chapter 2, low resolution cores were collected by a “vibra-coring” method wherein coring tubes were driven while being vibrated, enabled greater penetration of the sediments. This technique serves to partially liquefy the sediments around the tube walls, potentially permitting mixing between sediment layers. Once collected, low resolution core segments were rigorously homogenized so that the section was well represented in any subsample, such as that collected for PCB analysis. Cross-contamination of the magnitude of one percent would have little impact on the major goal of the program, *i.e.*, to establish current sediment inventories, since the amount of PCB represented in the deeper cross-contaminated layer would be roughly one percent of the total, well below the uncertainty of the PCB mass determination of the upper layers (26 to 36 percent based on the field split RPD). However, in the determination of the relationship of PCB mass and dechlorination, it has the potential to add significant variability to the data which is unrelated to the dechlorination process.

The issue of cross-contamination was avoided in the high resolution cores in several ways. Push coring, rather than “vibra-coring” was used. Thus less energy was available to mix adjacent layers. Additionally, instead of homogenizing each layer prior to subsampling, samples for PCB analysis were obtained by collecting a three-quarter-inch diameter mini-core from the center of each core slice. Because of the small size of the original 0.8 to 1.6-inch (2 to 4-cm) slice, subsampling in this manner integrated the slice thickness while avoiding any sediment layer mixing which may have occurred along the coring tube walls. Figure 3-6 illustrates the difference between the low resolution and high resolution subsampling processes.

To avoid the cross-contamination problem, it was decided to include only a portion of the low resolution coring results. Based on the measured presence of PCBs in all top core segments and the tendency for the PCB maximum to occur in this layer, all top segments were kept, regardless of the ^{137}Cs result for the bottom segment. This added 170 samples, one for each core. In addition, all core segments from cores with ^{137}Cs present in the bottom segment (*incomplete* cores as defined in Section 2.4.2) were included, which added 43 more samples. Lastly, the segment of maximum concentration in a core, if it was not the top layer, was added. This added 24 more samples, bringing the total to 237 out of a total of 371 core segments, or 64 percent of the data set. The remaining core layers were deemed to have too much potential for cross-contamination to be included here. All of the excluded segments failed the criteria given above. These samples met all of the following conditions:

- The segment was not the top-most segment in the core;
- The segment did not contain the maximum concentration for the core;
- ^{137}Cs was not detected in the bottom layer of the core, which indicated that the core was *complete* and had greater potential for cross-contamination since PCBs may not have been present in the bottom layer ; and
- The maximum PCB concentration for the core was found in a shallower segment, increasing the potential for cross-contamination of the lower layers as the coring tube was pushed down through the mud.

These criteria were sufficient to remove the vast majority of the widely scattered points. However, a few apparent outliers to the MW and MDPR vs total PCB regressions remained in the data set. Outliers were selected using the Mahalanobis distances (Mahalanobis, 1930) which are calculated for each point based on the mean, standard deviation and correlation for the data. All points that were excluded are points marked with an "X" on Figure 3-7. (A definition of Mahalanobis distances is given in the glossary.) Exclusion of these points yielded the final data set of 229 points, as shown in Figure 3-8, with the statistics for the final data set provided in the lower half of Table 3-2 (selected core segments). These results were compared with those in the upper half of the table (all core segments) to see the impact of removing the potentially cross-contaminated samples. The removal made almost no impact on the MW and MDPR, based on their mean and median values. The MW of the selected core segments had a geometric mean MW of 0.101, identical to that of the entire data set, with a median of 0.098 and a range of -0.106

to 0.195. This is notable since the mean total PCB concentration of the points doubled from 15.3 mg/kg to 31.8 mg/kg as a result of the selection process. This result would be expected given the removal from the data set of many relatively low level PCB samples whose congener patterns (and therefore MW and MDPR) matched those of the overlying, more contaminated core segments. That is, this would be expected if cross-contaminated samples are removed from the data set and not simply low level contaminated sediments which would presumably conform with the high resolution MW to total PCB relationship. The mean MW for the selected points corresponds to a mass loss of 12 percent, with no sample exceeding the theoretical limit MW of 0.223, derived in Table 4-8 of TAMS *et al.* (1997).

Removal of the potentially cross-contaminated samples from the data set examined here improves the general trend greatly, but still does not yield the regression line determined from the high resolution core data. Specifically, although the points tend to fall within the 95 percent confidence interval for individual measurements as defined by the high resolution cores, the low resolution core data are still shifted to the left of the regression line. In fact, a regression line fit to the low resolution core results was shown to be statistically different from the high resolution core regression (Figure 3-9), indicating a different relationship between dechlorination and total PCB mass in the two data sets. Chow's F test showed a greater than 99.99 percent probability that the coefficients of the two trends were different. This difference was primarily due to the intercept; slopes were similar (Butcher, 1998b). The difference between the two regression lines depends on whether MW or MDPR is used. At the mean conditions for the selected low resolution core segments (MW = 0.10 and MDPR = 0.54), the high resolution core regressions yielded a total PCB value of 107 mg/kg, 3.5 times higher than the mean low resolution core condition. This suggests that the low resolution core sediments have dechlorinated as if their concentrations were 3.5 times higher than the measured values.

This result was again disconcerting given that the two programs were measuring the same media in approximately the same manner spanning a period of less than two years. Further exploration of the PCB data and the sampling techniques was again warranted. As it turned out, the explanation again lay in the difference in sampling techniques.

For the high resolution cores, the 0.8 to 1.6-inch (2 to 4-cm) slicing intervals appear to have been small enough to capture one to five years of deposition. If we examine a typical high resolution core, we can see that changes in sediment PCB concentrations appear to be well captured by these sampling intervals. Figures 3-10 and 3-11 illustrate this point further by examining two individual high resolution cores. Based on the measured changes between adjacent core layers, it is evident that most high resolution core layers ought to be relatively homogeneous in concentration throughout their thickness. The only exceptions to this are the points around the PCB maxima where change is rapid and a given layer might span a concentration range of three. Conversely, the low resolution core slice or segment is nominally nine-inches thick. Given that the high resolution cores record the range of sediment concentrations deposited in a given area, it is likely that a low resolution core segment would span a range of two or more orders of magnitude, based on the PCB ranges measured in the high resolution cores over a nine-inch interval. If we then apply the total PCB versus MW and MDPR relationships derived from the high resolution cores, it is apparent that the PCBs contained in a low resolution core segment would have seen a broad range of dechlorination conditions. However, the process of collecting and homogenizing the low resolution core sample would serve to effectively dilute the concentrated and dechlorinated layers with the less concentrated, relatively unaltered layers, found above and below the PCB maximum. The dilution would modify the measured concentration but have little effect on the MW and MDPR since these parameters represent congener ratios, which tend to be unaffected by dilution. The congener ratios would be unaffected because of the large PCB mass represented by the peak concentration layers. The collection and homogenization process would effectively yield a relatively dilute sample with the level of dechlorination normally found in a concentrated layer as measured by the MW or MDPR. In Figure 3-9, this would serve to shift the MW and MDPR relationship with total PCB to the left relative of the high resolution regression, just as it is plotted. The extent of the shift would depend upon the range of concentrations contained within a given low resolution core segment; the greater the range, the greater the shift. Presumably, the shift would be greatest for cores where sediment deposition was undisturbed by biological processes, yielding a range of values akin to those seen in the high resolution cores. Conversely, vertical mixing by biological or other processes would minimize this effect. A similar effect would be obtained for a core segment which contained portions of pre- and post-1954 sediment, wherein the uncontaminated layers would serve to dilute the overlying contaminated ones without changing the MW and MDPR values.

To further illustrate this point, we can examine the two high resolution cores presented in Figures 3-10 and 3-11, that differ by about an order of magnitude. Assuming that the cores in the figure were each represented by a single low resolution core segment, the length-weighted average concentration of the full core (that which would be obtained by a thorough homogenization of the core) of Core 19 (Figure 3-10) would be 512 mg/kg (ppm) with a MW of 0.1871 and an MDPR of 0.8828. This is to be contrasted against the conditions of the high resolution core PCB maximum concentration layer of 2,083 mg/kg (ppm) with a MW of 0.2074 and an MDPR of 0.9156. Calculating the MDPR and MW from the original high resolution core regression line ($\text{MDPR} = -0.714 + 0.248 \log [\text{Total PCBs}]$ and $\text{MW} = -0.251 + 0.070 \log [\text{Total PCBs}]$) using the homogenized concentration of 512 mg/kg, we obtain an MDPR of -0.0421 and a MW of -0.0614, substantially lower than the length-weighted average values. Based on the high resolution core regression line, the MW value obtained for the calculated low resolution core concentration corresponds to a concentration of 1,814 mg/kg (ppm) or about 3.5 times higher than the calculated concentration. Note that this increase is in accordance with the difference between the high resolution core and the low resolution core regressions shown in Figure 3-9.

For High Resolution Core 21 (Figure 3-11) the length-weighted average would be 66 mg/kg (ppm) with a MW of 0.1639 and an MDPR of 0.7325. This is to be contrasted against the conditions of the PCB maximum concentration layer of 260 mg/kg (ppm) with a MW of 0.1945 and an MDPR of 0.8682. Calculating the MDPR and MW from the original high resolution core regression line using the homogenized concentration of 66 mg/kg, we obtain an MDPR of -0.2628 and a MW of -0.1236, substantially lower than the length-weighted average values. Based on the high resolution core regression line, the MW value obtained for the calculated low resolution core corresponds to a total PCB concentration of 845 mg/kg or about 13 times higher than the calculated concentration.

In fact, this calculation was done for all the high resolution cores of the Upper Hudson. The results are illustrated in Figure 3-12. In this diagram, it is evident that if the high resolution cores had been collected as low resolution cores, the resulting relationship between the degree of dechlorination as measured by MW or MDPR and the total PCB concentration would be shifted to the left by a factor of five- to eight-fold relative to the high resolution sediment core regression

line. That is, concentrations would be five to eight times lower to achieve a given level of dechlorination. Based on the relationships determined for the high resolution and low resolution coring programs, it is evident that any coring study which fails to consider the degree of vertical variability within the sediment will overestimate the extent of dechlorination that can be anticipated for a given sediment concentration.

The impact of vertical homogenization has different impacts depending upon the concentration range in the sediments being collected. Areas of high sediment variability and high sediment inventory, such as *hot spot* areas, will yield a greater degree of dechlorination than would be predicted from the measured concentration over a large vertical interval. This is because the most concentrated layers with correspondingly high levels of dechlorination will be diluted by the sampling process while the internal measures of dechlorination (MDPR and MW) will not be affected. Conversely, in sediments of relatively low contamination, such as those found in the extensive areas of coarse sediments, the sampling process will have little effect and these samples will match the trend obtained from the high resolution cores. This is evident in the extent of scatter in Figure 3-9. Specifically, the range of the low resolution core results includes the mean trend (the regression line) from the high resolution cores. In addition, the scatter associated with the low resolution cores ($R^2 = 0.65$ for MW and total PCBs) is greater than that for the high resolution cores ($R^2 = 0.73$), as would be expected due to sample homogenization.

In summary, the low resolution core results are consistent with the conclusions drawn from the high resolution cores concerning dechlorination and PCB mass. The low resolution cores closely replicate the relationship between MW and MDPR, confirming the occurrence of meta- and para-dechlorination and the absence of ortho-dechlorination. Due to several issues concerning low resolution sediment core collection, specifically vertical homogenization and potential cross-contamination, the relationship between dechlorination and total PCB mass appears somewhat different in the low resolution core results. However, when these issues are factored in to the examination of the data, the conclusions drawn from the high resolution cores concerning dechlorination are confirmed by the low resolution core results.

3.2 Interpretation of the Relationships Among the Low Resolution Core Parameters

This section describes the relationships found among total PCBs and other measured parameters. The main purpose of this examination is to assess which parameters may be useful in predicting sediment PCB inventories. In addition, the examination will assess the degree to which PCBs found in Hudson River sediments conform to general expectations of PCB behavior in the environment. The analyses in this section are expected to show limited relationships because PCBs, as well as other parameters, most likely vary over narrower depth segments than sampled in the low resolution coring program.

The type and number of parameters collected during the low resolution coring program are outlined in Chapter 2. The parameters themselves can be classified according to type as shown in Table 3-1. Nearly all possible parameter pair relationships were examined for this report. The notable exceptions are the congener-specific and homologue data which were excluded from this analysis. This exclusion was made so as to maintain the major focus of this report, *i.e.*, an examination of sediment PCB inventories warranting use of total PCB concentrations. PCB congener pattern matching or 'fingerprinting' was discussed at length in the previous Phase 2 DEIR (TAMS *et al.*, 1997) and is not covered here.

The relationships among most of the parameters in Table 3-1 were initially examined on a regression-basis, that is, regression plots and regression coefficients were generated for the various parameter pairs. These results aided in the selection of parameter pairs for further exploration. In addition, several parameters were examined based on their expected influences on PCB concentration.

Using selected samples based on criteria described in Section 3.1, the total PCB concentration more than doubled to 31.8 mg/kg (Table 3-2). This increase resulted from focusing on *hot spots* and more contaminated sediments. Despite removing lowest level samples, which resulted in an increase in the mean PCB concentration, the 12 percent mass loss by dechlorination remained constant because cross-contaminated samples were scattered over the range of MW.

Cross-contamination occurred when recent deposition was shallow (0 to 12-inches) and deeper slices were obtained, independent of the level of PCB contamination in the sediment itself.

The results of the initial regression analyses are presented in Tables 3-3 to 3-8. The first table represents a correlation matrix for the entire suite of Laser grain-size distribution parameters. This large table demonstrates the strong correlations among many of these parameters, as would be expected since many of the parameters represent similar properties. For example, silt % is strongly correlated with the phi 4.5 to 7 (r greater than 0.8). These phi fractions represent sediments in the silt classification (diameters 44 to 7 μ m, respectively). Similarly silt % is inversely correlated with fine sand % as might be expected since as the fraction of silt % increases, the fraction of other classes would be expected to decrease. The strong correlations among many of these parameters indicates that only a limited suite of them are required to represent the grain-size characteristics. The next four tables summarize the relationships between three PCB measures (total PCB concentration, change in molecular weight relative to Aroclor 1242 (Δ MW), and MDPR) and Laser grain-size distribution parameters, ASTM grain-size distribution parameters, radionuclide parameters, and bulk sediment properties (Tables 3-4, 3-5, 3-6, and 3-7, respectively). The number of samples represented in a table is equal to the number of samples that remained in each analysis after outliers were excluded using a Mahalanobis analysis (Mahalanobis, 1930). For example, in Table 3-4, the 170 top core segments were examined for grain-size distribution parameters, using Laser grain-size methodology, and for PCBs, but only 136 to 149 of the samples were considered acceptable. Similarly, of the 143 core segments taken from various depths and run for ASTM (sieve) analysis between 122 to 130 were considered to be within acceptable ranges (Table 3-5). In each table, regression coefficients for each parameter *vs* total PCBs, Δ MW, and MDPR are presented. In general, parameters describing the fine-grained properties of the sediment showed the strongest correlations with total PCBs although few exhibited strong predictive power (r greater than 0.5). The notable exceptions were the sediment density-related properties which had r values around 0.6 for shallow sediments, as shown in Table 3-7. Also notable is the generally stronger correlations seen between total PCBs and the Laser analysis parameters relative to those for the ASTM analyses. This was attributed to the fact that the Laser analyses were performed on the shallow sediments exclusively, where the majority of the sediment PCB inventory was found. The parameters Δ MW and MDPR are included in each table to examine the correlation between the extent of dechlorination and parameters other than total PCB concentration. The relationship

between total PCB concentration and the degree of dechlorination as measured by MW and MDPR was discussed extensively in the previous section.

In the last regression result table (Table 3-8), the more highly correlative variables from the previous four tables are compared with the two integrated PCB parameters. Specifically, PCB mass per unit area and the core length-weighted average PCB concentration are compared with bulk density, percent solids, percent silt, and ¹³⁷Cs. In these tables, the non-PCB parameters represent the properties of the shallow (0 to 9-inch) or surficial (0 to 1-inch) sediment layers.

Evident in Tables 3-4 to 3-8 is the generally weak correlation among the PCB measurements and the other parameters. Regression coefficients are rarely higher than 0.5, indicating only weak predictive power. The regression of the two integrated variables provided the highest level of correlation (Table 3-8). In addition, PCB inventories tended to be greater towards the surface, thereby resulting in higher correlation coefficients. Percent silt had the strongest correlation (0.35) of the major soil classifications, but the mean phi regression coefficient was also 0.35, with phi 4.5 to phi 6.5 (*i.e.*, samples classified as silts) having the highest correlations (Table 3-4). None of the D(x) parameters were particularly strong although the regression coefficients were comparable to the other grain size parameters (Table 3-4). The D(x) parameters represent the effective diameter in millimeters of a sieve which would retain "x" percentage of the sample mass. Thus, the d(50) is the approximate median particle diameter and the d(15) and d(90) represent the coarsest and finest fractions of the sample. Additional discussions on the relationship between the two different grain size distribution methods used in the Low Resolution Coring program are presented later in this section. In the discussions and figures to follow, the median phi (the median diameter on the phi scale) is used to represent the class of Laser-based parameters.

Confirmation of Regression Analyses

After completing the initial regression analysis, the better regression pairs were examined in more detail, as discussed below. The comparisons were made by grouping or binning the non-PCB parameters into equally spaced bins, generally with a sufficient number of values (at least eight if at all possible) to permit the accurate calculation of a mean and standard deviation. The mean PCB concentration in logspace for each of the bins were then compared to each other using a Tukey-Kramer honestly significant difference calculation (Box *et al.*, 1978) at the 95 percent confidence level to test for differences among the bins and confirm the regression analysis. This test permitted identification of those trends of PCBs and parameters which were statistically significant. Log-transformed total PCB concentration data were used in these analyses since the PCB data were found to be log-normally distributed, as discussed in Chapter 2.

Outliers to the regression analyses were examined when apparent, based on regression plots of each parameter pair (*e.g.*, total PCB and bulk density). A Mahalanobis test was performed to identify the outliers which were eliminated from the regression analysis. The regression results presented in the tables and figures of Section 3-2 do not include the identified outliers.

The data presented in the figures of this section are represented in a “box and whisker” format. Essentially, the data for PCBs are binned according to the variable on the x-axis and then represented by a series of box-and-whisker plots. Each box encloses 50 percent of the data with the median value of the variable displayed as a line. The top and bottom of the box mark the limits of the central 50 percent of the variable population. The lines extending from the top and bottom of each box mark the minimum and maximum values that fall within an acceptable range. Any value outside of this range, called an outlier, is displayed as an individual point. The box diagram describes the following statistics for the data set:

Median	The data value located halfway between the smallest and largest values.
Upper Quartile (UQ)	The data value located halfway between the median and the highest data value (top of box).

Lower Quartile (LQ)	The data value located halfway between the median and the lowest data value (bottom of box).
Interquartile Distance (IQD)	The distance between the Upper and Lower Quartiles (UQ - LQ).
Range	The minimum and maximum values of the data set that fall within $UQ + 1.5 * IQD$ and $LQ - 1.5 * IQD$
Outliers	Points whose value is either greater than $UQ + 1.5 * IQD$ or less than $LQ - 1.5 * IQD$

Note that the identification of outliers by the box-and-whisker plot is not the basis for the exclusion of points from the regression analysis. Only those points identified by the Mahalanobis test mentioned above are excluded from the regression analysis. The plots presented in this section include all points, including the outliers.

For the comparisons of the various parameters with PCB concentration, the vertical axis, representing total PCB concentration, is always in log-scale. This is based on the analysis presented previously which showed the PCB concentrations to be log-normally distributed. Thus, the correlations are all made to the log of the PCB concentration since this is a relatively constant parameter to which the standard statistical assumptions concerning normality can be applied.

In addition to the box-and-whisker diagrams for each data bin or group, the data bin median and arithmetic mean are shown. The median corresponds closely to the geometric mean since the PCB data are log-normally distributed. The arithmetic average is calculated on the actual PCB concentrations and not on the log-transformed data.

Correlation with Bulk Sediment Properties

Figures 3-13 to 3-18 and Table 3-7 show various comparisons between the PCB measures and the bulk sediment properties. Total PCB concentrations were found to generally decline as the

bulk density, percent solids, solid specific weight and particle density increase. This would be expected assuming that the organic carbon content declines as these parameters increase. This was confirmed for bulk density and percent solids for both shallow sediment samples and all sediment samples. Most bins from the sediment samples were found to have statistically different mean values from at least half of the other bins in the diagram. In general, the relationship to total PCBs was found to be stronger in the shallow sediments. This is attributed to the constant presence of PCB in this layer. When the deeper layers are included, layers with similar bulk properties but little PCB mass are added (typically the deepest layers), thus adding scatter to the data and weakening the correlations.

For solid specific weight (the product of bulk density and percent solids), the trend was much weaker and typically only the end bins were statistically different from the rest of the set. Similarly, particle density did not show any statistical significance with respect to total PCB concentrations based on the binned data. This was somewhat unexpected but is probably the result of the calculation of particle density which involves both bulk density and percent solids. It is likely that the combined uncertainty of these two parameters as particle density creates too much total uncertainty and prevents the detection of a statistically significant trend.

In Figures 3-17a and 3-17b, bulk density is compared with the measures for dechlorination (MW and MDPR) for all sediments and shallow sediments, respectively. The MW and MDPR both decline with increasing bulk density. The correlation with shallow sediments and measures of dechlorinations is greater than the correlation with all sediments and is attributable to the constant presence of PCBs in the shallow layer. Regression coefficients for these parameters are shown in Table 3-7. This is the same trend found for total PCB mass. However, given the weakness of the regressions with bulk density, it is likely that the trend is the result of the strong correlation among total PCBs, MW and MDPR, and not related to any change in bulk density.

In summary, these results show the dependence of total PCB concentration on the presence of lighter material in the sediment (*e.g.*, Table 3-6, Regression Coefficients). Presumably this lighter material represents organic matter. The correlation of MW and MDPR values is largely a ramification of the correlation with total PCB. None of the bulk sediment parameters are better

predictors of the extent of dechlorination than total PCB concentration. Among the four bulk sediment parameters, percent solids had the strongest correlation with total PCBs.

Correlation with Grain Size Distribution

Three different measures were available to describe the grain-size distribution of the sediment samples: Laser analysis, ASTM (sieve) analysis, and the geologist's visual classification. In general, the parameters generated by these techniques exhibited weaker correlations for the laser analysis (Table 3-4) and the ASTM analysis (Table 3-5) than the bulk sediment parameters (Table 3-7) described above. All three techniques generated a principle grain-size fraction parameter. The comparison among these results for principle fraction was presented in Section 2.4.3. In comparing the principle fraction to total PCB content, each technique produced a consistent finding that samples classified with silt (or fines) as the principle fraction had a substantively higher PCB content relative to the other sediment classes.

Using the geologist's classification and the Laser technique results, the silt group was statistically higher than all other groups, with approximately a four-fold higher PCB concentration. The coarser sediment classes, fine-sands and coarse sand/gravel, were not statistically different from one another, based on the Tukey-Kramer honestly significant difference at the 95 percent confidence level. Figure 3-18 shows the relationship between principle fraction by geologist's visual inspection versus total PCB concentration. Diagrams are shown for all sediments and for shallow sediments. The diagram for all sediments represents all 371 measurements since all samples analyzed for PCBs were also classified by the field geologist.

The PCB results support the widely held theory that PCBs tend to associate with fine-grained sediments. Also notable in Figure 3-18 are the distinctly low values for clay samples. These samples were identified as clay by the geologist, although subsequent grain-size analysis later classified them as silts. However, the nature of these "clay" samples was distinct from fine-grained sediments found elsewhere in the river. Specifically, the clay samples were distinctly gray in color with visible banding typically associated with varves. These samples were believed to represent lake bottom deposits from a glacial-age lake resulting in their low level of PCB

contamination and failure to conform with the expected trend of fine-grained sediment and higher PCB content.

The ASTM grain-size distribution data, while confirming the general finding of higher PCB levels in samples whose principle fraction was silt, did not yield as much statistical separation among the various sediment classes as the two other methods. In addition, as a whole, the ASTM samples were less contaminated than the shallow sediment Laser samples (geometric means for total PCBs of 7.0 and 23.4 ppm, respectively). The lessened statistical significance and the lower average PCB level were attributed to the fact that the ASTM sample data set consisted of many samples collected at depth (second and third core segments) where PCB concentrations were typically lower, regardless of sediment type. Presumably, a portion of these sediments would include PCB-free material deposited prior to 1950 which would exhibit no correlation between PCB content and sediment type.

Since the silt classification proved to be a statistically significant predictor for PCB, it was explored further on a quantitative basis as percent silt. This analysis could only be done for the Laser and ASTM technique results which had quantitative results. Figure 3-19 shows the results for percent silt vs total PCB concentration for the Laser analysis. This figure represents the data from all 170 top segments (shallow sediments). The Laser results were chosen for this presentation because they represent shallow sediments exclusively where most of the PCB mass is found. Sorting the percent silt data into three groups yielded three statistically different means showing the predictive power of this parameter. The results show a relatively steady increase to higher PCB levels with higher silt content. The sediments with silt fractions greater than 66 percent were on average five times higher in PCB content than sediments less than 33 percent silt.

The last parameter to be examined under grain-size distribution is the mean phi (ϕ). The parameter phi is a measure of the particle diameter calculated as follows:

$$= -\log_2 (\text{diameter in mm}) \quad (3-4)$$

Thus, each unit of phi represents a halving of the particle diameter (*e.g.*, 8 phi equals 0.0039 mm, which equals half of 7 phi at 0.0078 mm). Mean phi is a measure of the center of the sample's grain-size distribution, unlike percent silt which is more a measure of the sample mass than a measure of specific diameter. It should be noted that phi is a negative log value and thus as the phi value increases, the particle diameter decreases. Figure 3-20 groups total PCBs by mean phi and exhibits a trend to higher PCB levels with higher phi. However, only the rightmost bin, representing sediment samples whose mean diameter is less than 4.5 phi or 0.044 mm (44 μm ; *i.e.* samples classified as silt), is statistically significant from the others.

In summary the grain-size distribution data showed the expected correlation of PCBs and fine-grained sediments but little more. The parameters generally showed a slightly weaker correlation (absolute value of r , $|r|$, was between 0.41 and 0.47 for phi 4.5 to phi 6) with total PCBs than the bulk sediment properties ($|r| = 0.50$ to 0.58). Similarly, the correlations between MW, MDPR and the grain-size parameters ($|r| = 0.36$ to 0.43) were lower than those for MW, MDPR and the bulk sediment properties ($|r|$ for MDPR = 0.40 to 0.54) for shallow sediments. It would appear that correlations between total PCB concentration and both the grain-size distribution data and the bulk property data are concurrently tracking the fine-grained, rich-in-organic matter silt content of the sediment and little else.

Chemical and Radionuclide Parameters

Six parameters were examined under this heading. Three, consisting of total organic carbon (TOC), total kjeldahl nitrogen (TKN), and the carbon-to-nitrogen molar ratio (C/N), were conducted on a very limited data set (27 samples) and thus are limited with regard to correlation analysis. The C/N ratio is the molar ratio of the TOC and TKN analyses. As noted in Section 2.3.3, TOC and TKN were obtained from a very limited sample set. The samples were randomly selected from the set of core segment samples and were originally intended to merely confirm the results of the total carbon/total nitrogen analyses which were never completed. The other three parameters, surficial ^{137}Cs , surficial ^7Be , and bottom segment ^{137}Cs , were not measured on samples run for PCB analysis and cannot be considered on an individual sample basis. These parameters are descriptive of the core as a whole, without a direct connection to any individual sample. For this reason, the ^{137}Cs and ^7Be results were compared to the entire core inventory as PCBs per unit area. In addition, surficial ^{137}Cs and ^7Be were also compared with the corresponding core shallow segments since they partly overlapped. The regression results for these parameters vs total PCB, MW, and MDPR are summarized in Table 3-6.

The TOC, TKN, and C/N ratio generally exhibited only weak correlations with total PCBs, MW, and MDPR. PCB concentration showed a positive correlation with TOC as would be expected although the correlation was weak ($r = 0.39$). The relationship between TOC and total PCB is shown in Figure 3-21. Most of the response between TOC and total PCB concentration occurs between those with samples less than three percent TOC and those greater than three percent TOC, although none of the groups displayed in Figure 3-21 were statistically different from the others. Few samples had concentrations below three percent, which made it more difficult to determine statistical significance.

TKN exhibited a slightly weaker correlation with total PCB than TOC and consequently was not examined further. The C/N ratio exhibited a weaker relationship with total PCB ($r = 0.29$) than either of the individual measurements. Interestingly, the C/N ratio showed a relatively strong correlation with the dechlorination measures MW and MDPR ($r = 0.36$ for both) as compared to the individual TOC and TKN relationships ($|r| < 0.2$). Changes in the C/N ratio are believed to be reflective of increases in the wood cellulose content of the sample, which would increase the molar

C/N ratio. As discussed previously, soil and algal-based organics would be expected to have C/N ratios around 10 while wood-based materials can have values greater than 100. Wood cellulose would be presumably derived from wood chips. The suggestion that the degree of dechlorination increases with the C/N ratio would indicate that the presence of woody materials correlate with high PCB concentrations in the sediment. Unfortunately, the visible presence of wood chips did not correlate with the C/N ratio, as noted in Section 2.4.3, so no visual clue could be confirmed for the possible occurrence of dechlorination. However, this data set is limited in the number of samples represented and so further exploration of these issues is not possible.

The radionuclide results showed several significant correlations with the PCB parameters, such as between ^{137}Cs in surficial sediments and PCB concentrations in the corresponding shallow sediments ($r = 0.45$). ^7Be measurements in surficial sediments were shown to have a statistically significant relationship with shallow sediment PCB concentrations when grouped into ^7Be detected and non-detected groups. The median total PCB concentrations were about three times higher for the sediments when ^7Be was detected, indicating that PCB concentrations in shallow sediments were higher in areas showing recent deposition. No correlations between ^7Be concentrations and sediment PCB concentrations were found, other than the detect/non-detect groupings. Similar but weaker results were found when the data for PCB mass per unit area were examined (see Figure 3-22 and Table 3-6). Although the presence of ^7Be was shown to correlate with higher PCB concentrations, this should not be assumed to result from recent deposition of PCBs from recent GE releases, effectively increasing the inventory. As will be discussed in Section 4.1 the majority of sites studied exhibited PCB mass loss relative to previous studies. If recent deposition is relatively contaminated as compared to prior deposition, its impact is undiscernible given the vertical resolution obtained for these cores and the estimated net PCB losses. Thus, ^7Be presence is correlated with relatively higher PCB inventories but is not necessarily evidence of recent deposits of highly contaminated material. Nonetheless, since all locations had measurable levels of ^{137}Cs and PCBs, the following inferences can be made:

1. The presence of ^{137}Cs and PCBs indicates that all sites cored were depositional at least at one point in the last 40 years.
2. The sites without ^7Be present are not currently accumulating sediment and therefore are probably not being buried.

3. The lower PCB concentrations in the ^7Be non-detect cores indicate that either less PCBs were deposited at these sites to begin with or that PCB loss, potentially via scour, has occurred, or both.

While the inverse correlation between ^7Be absence and PCB concentration does not offer proof of sediment scour, it does suggest that burial of contaminated sediments with “clean” sediments is not occurring in at least 30 percent of the coring sites since there is no evidence of recent burial.

^{137}Cs was measured in both surficial and bottom core sediments. Both measurements were compared with total PCB concentration and inventory. ^{137}Cs in core bottoms had no statistical correlation with sediment PCB concentration or inventory. This suggests that the *incomplete* cores described in Chapter 2 can probably be considered good estimates of the current PCB inventory at their coring sites. Notable exceptions are discussed in Section 4.2. However, as a predictor for PCB concentration or the degree of dechlorination, ^{137}Cs was not useful.

^{137}Cs in surficial sediments exhibited the strongest correlations with PCBs of any of the radionuclide measurements. Table 3-6 contains the regression coefficients for ^{137}Cs in surficial sediments. The relatively strong positive correlation of ^{137}Cs with shallow sediment PCB concentration is shown in Figure 3-23. The data can be grouped into three statistically significantly different groups 0 - 500 pCi/kg, 500 - 1,000 pCi/kg and >1,000 pCi/kg. The two highest ^{137}Cs bins (1,000 - 1,500 pCi/kg and 1,500 - 8,000 pCi/kg) are statistically indistinguishable. These data support the anticipated association of PCB and ^{137}Cs . Although they have different release histories, their association with fine-grained sediments yields a positive correlation between them. In addition, the thick low resolution core segments tend to span a sufficient depositional interval (roughly 30 to 40 years), so as to average-out their different histories and yield a positive correlation. Interestingly, the three-fold range in ^{137}Cs concentration yields an order of magnitude increase in the PCB concentration in surface sediments. The range of ^{137}Cs obtained for the low resolution core surficial sediments (44 - 8700 pCi/kg) is greater than that obtained for the high resolution core surficial sediments (250 - 1300 pCi/kg) but only three samples exceeded 2000 pCi/kg. In fact, the median value for the low resolution surficial sediments was 715 pCi/kg, well

within the range of the surficial sediments for the high resolution cores. Given the varied sediment types and varied depositional environments sampled under the low resolution coring program, which would serve to deposit, accumulate and rework sediments of various ^{137}Cs levels, the range of the ^{137}Cs levels measured in the surficial sediments does not appear extraordinary.

^{137}Cs was also positively correlated with the sediment PCB inventory as would be expected given the correlation with surface concentration. The PCB inventory data exhibited more variability with surface ^{137}Cs but still showed at least an order of magnitude increase across the range of ^{137}Cs values.

^{137}Cs in surficial sediments was also compared with the MDPR and MW to examine the relationship between ^{137}Cs and dechlorination. Both the shallow sediment MDPR and MW as well as a core average MDPR and MW were examined against ^{137}Cs . The core averages of MDPR and MW were calculated using length-weighted average congener concentrations. All dechlorination measures were positively correlated with ^{137}Cs . The MW and MDPR for shallow sediments are plotted in Figure 3-24. Although positively correlated, the regression coefficients are weaker than those between PCB concentration and surface ^{137}Cs , indicating that the correlation between ^{137}Cs and dechlorination is merely a result of the correlation between ^{137}Cs and total PCB concentration and the far stronger correlation between dechlorination and sediment PCB concentration. As in all the other variables examined, the correlations using the entire core were weaker than those for the shallow core segments alone.

Summary

Correlation analysis among the various parameters and the PCB measures generally confirmed the expected relationships for PCBs in the environment. The strongest predictors for log-transformed, length-averaged PCB concentration among the parameters examined were percent solids, solid specific weight and bulk density, all of which were negatively correlated with concentration. This was anticipated, given that at lower density, more porous sediments tend to be richer in organic matter and fine-grained sediments, which also have an affinity for PCBs. PCB concentrations were positively correlated with fine-grained sediment as measured by the principle sediment fraction, the percent silt, or the median diameter. Several phi fractions, phi 4.5, phi 5, phi 5.5, phi 6 and phi 6.5, exhibited stronger correlations than the three more general sediment grain-size parameters just listed. These phi fractions correspond to particle sizes in the range of 11 to 44 μm , which are all contained within the silt fraction (5 to 75 μm). Correlation coefficients were in the range of 0.41 to 0.47, which were still substantively lower than those for the bulk sediment properties ($|r| = 0.56$ to 0.65). The other phi fractions and the fractional diameters, D(10) to D(99), did not prove any more useful in predicting PCB concentrations than did the more general grain-size parameters such as percent silt and median diameter.

PCB concentrations were also positively correlated with organic carbon (TOC) although the data set was quite limited, preventing a more thorough examination of the relationship. The degree of dechlorination, as measured by MW, was positively correlated with the C/N ratio, suggesting that sediments high in wood materials exhibit higher degrees of dechlorination. This correlation may be the result of the higher PCB concentrations which have been demonstrated for wood chip-bearing layers (Bopp and Simpson, 1989).

Correlation analysis between PCBs and the radionuclide measures yielded some interesting findings. Although the ^{137}Cs measurement on the bottom-most core segment did not yield any statistical correlations, both surficial ^7Be and ^{137}Cs did. ^7Be was used on a detect/non-detect basis and PCB concentrations were higher by a factor of three in samples in which ^7Be was detected, as compared to samples where ^7Be was not detected. The absence of ^7Be in approximately one-third (30%) of the cores indicates the lack of sediment burial in these coring sites and their potential as active scouring sites.

Surficial ^{137}Cs was shown to positively correlate with the shallow sediment PCB concentration, the sediment PCB inventory, the degree of dechlorination in shallow-sediments (MW and MDPR) and the degree of dechlorination in the entire core. The first two correlations were expected, given that both PCBs and ^{137}Cs preferentially adsorb to the same sediment type. The latter two correlations are believed to stem from the strong correlation between dechlorination and PCB concentration and do not represent an independent correlation between dechlorination and ^{137}Cs .

In all of the correlation analyses, shallow sediments always provided stronger correlations between the variables than did the results for the entire core. This was attributed to the fact that most of the cores' PCB maxima occurred in the shallow sediment (top) segment, and most of the PCB inventory was found in the upper 9 inches of sediments. In addition, the inclusion of the deeper layers in the correlation analysis meant the likely inclusion of sediments deposited prior to the PCB discharges by GE, sediments whose properties would have no correlation with PCBs. Thus, the whole core correlations were weakened relative to shallow sediments.

The correlation analyses confirmed the expected behavior of PCBs in the Hudson River environment. PCBs are most concentrated in fine-grained, relatively low density, probably organic-rich sediments with relatively high levels of ^{137}Cs . Dechlorination correlates with a number of variables but none are as useful for predicting dechlorination as the PCB concentration itself.

3.3 Interpretation of the Low Resolution Core and the Side-Scan Sonar Results

An important intended use of the low resolution coring results was their application to the side-scan sonar data collected in 1992 and initially reported in the Phase 2 Volume 2C Data Evaluation and Interpretation Report (TAMS *et al.*, 1997). In this section the application of both the grain-size distribution data and the sediment PCB concentrations obtained during the low resolution core sampling program are compared with the prior results reported in the DEIR. While a large concurrent grain-size distribution data set (the confirmatory sediment samples) was originally available to calibrate the side-scan sonar data, the PCB data in the DEIR analysis were not concurrent, having been collected in 1984 by NYSDEC. Thus, the analysis of the low resolution core sediment PCB data will provide a relationship for current conditions. In addition, the low resolution core data set extends below the TI Dam, and so provides data on current conditions over a longer distance than the original 1984 data set.

Generation of the Digital Number Values (DNs) for Low Resolution Coring Sites

To apply the low resolution core data to the side-scan sonar results, it was first necessary to obtain the arithmetic mean acoustic response, or digital number, for each of the low resolution sampling sites. The arithmetic mean digital number (DN) was obtained for both 10- and 50-foot circles circumscribed about each sampling point based on the 500 kilohertz (kHz) acoustic signal images, the primary side-scan sonar results. In the analysis of the side-scan sonar data in the DEIR, both the arithmetic mean and the median DN50 were examined and shown to yield similar results. In this analysis only the arithmetic mean was examined since it was found to yield slightly better correlations relative to the median. The DN10 and DN50 represents the average of all acoustic results contained in the 10- and 50-foot circles, approximately 82 and 1900 points per circle, respectively. The results for the 50-foot circle (DN50) were used in all of the subsequent analyses described here. Both 50-foot and 10-foot circles were used in the analyses reported in the DEIR. Figure 3-25 shows the general relationship between the DN50 and the DN10 for the low resolution sites selected for use in this analysis. Although some scatter is evident in the relationship between the two DN values, a regression on the data is relatively close to the ideal match. At the upper end of the range, the difference between the DN50 and DN10 is only 15 percent. The selection criteria for the low resolution core sites is described immediately below.

As part of the calculation of the DN50, the quality of the acoustic image around each sampling point had to be reviewed. This was accomplished using a geographical information system to coordinate sample locations, the 50-foot circles, and the side-scan sonar images themselves. Plates 3-1 to 3-19 are the side-scan sonar image maps showing the locations of the low resolution core sites and their associated circles. Of the 170 core sites, only 119 were located in areas covered by the side-scan sonar images. Of the 119 locations, 26 locations had to be excluded due to image quality issues. Many points had to be excluded due to proximity to the edge of the image. The entire 50-foot circle had to be within the sonar coverage or else false values would be included in the DN50 calculation. Other locations were excluded simply due to poor image quality, typically the occurrence of the ship's track within the 50-foot circle. To confirm the visual choices of poor image quality, the DN50 and DN10 values were compared. Good quality images would have similar values for both DNs. This is shown in Figure 3-25 which is a plot of the DN50 vs DN10 for the final point selection: Poor quality images would fall far from the ideal line shown in Figure 3-25. The selection process yielded 93 locations whose associated images, within the circle, were acceptable. These locations are marked on Plates 3-1 to 3-19 by a 50-foot circle. Excluded locations are marked with a circle overwritten with an 'X'. It is important to note that in the production of these plates, some image quality was sacrificed in order to fit the images on the 8-1/2 by 14-inch sheets. In selecting acceptable locations, the original side-scan sonar images were examined at their original size and scale.

Application of the Low Resolution Core Grain Size Distribution Data to the Side-Scan Sonar Images

The DN50 values obtained for the low resolution coring sites were then compared with the Laser grain-size distribution parameters obtained on top (shallow) core segments using least squares linear regressions. These regression results were then compared with the confirmatory sampling program results on the basis of the correlation coefficient (r) term (See Figure 3-26). In general, both the low resolution and confirmatory sampling data sets show relatively strong correlations ($r > 0.38$) for the same grain-size distribution parameters. Nonetheless, the low resolution core results generally yielded lower r values. For example, the r value for the mean phi (ϕ) (geometric mean diameter) for the low resolution coring results was 0.68 as compared to 0.73 for the confirmatory cores. Similarly, the correlation with percent silt plus clay at 0.64 was less than that for the confirmatory samples at 0.73. Only percent sand and percent gravel had higher correlations for the low resolution cores relative to the confirmatory cores. The precise reason for the general decrease in correlation is not known; however, it is likely that it stems from several differences between the two programs. In particular, the low resolution core sediment grain-size distribution parameters were obtained for shallow sediments, nominally from 0 to 9-inches in depth. Confirmatory sediment samples were obtained from core tops from 0 to 2-inches in depth and from shallow grab samples approximately 4 to 6-inches in depth. Thus, the confirmatory samples would more closely measure the actual sediments (*i.e.*, surface sediments) responsible for the acoustic signal at a given location. In addition to the difference in sampling technique, the orientation of the two programs was different. For the confirmatory sampling programs, the intent was to obtain samples from many different sediment types so as to calibrate the side-scan sonar results. The low resolution cores were intended to characterize sediments in a limited number of areas focusing on regions of high PCB inventory. In this manner, the low resolution program did not obtain many coarser-grained sediment samples. The lack of these data might serve to weaken the strength of the regressions. Lastly, it is also possible that there were some changes in sediment type at some locations. However, as will be discussed below, there does not appear to be any extensive changes in sediment type.

In addition to the regression comparisons, the low resolution core data were also compared with the side-scan sonar images on the basis of sediment type. For each of the top low resolution core segments, a principal sediment class was identified by both visual inspection and by Laser analysis. Similarly, the image areas had been classified as to the general sediment type based on the image itself. The comparison between the two sediment classification techniques and the side-scan sonar classifications are shown in Figure 3-27. It is evident from the two diagrams that the results for the Laser analysis correspond better than the visual inspection with the side-scan sonar interpretation, although both techniques agree well with the side-scan sonar classifications. Note for example, the greater correspondence of the silt samples by Laser analyses with the fine-sediments classification by side-scan sonar. The reason for the better agreement between side-scan sonar and Laser analysis is not known but probably results from the more accurate classification by the Laser technique. Also, the original side-scan sonar interpretations were based on Laser analysis of the confirmatory sediment samples. For this reason, the remaining discussion on the correspondence between sediment sample classifications and side-scan sonar results will discuss the Laser results exclusively. It should be noted that all of the low resolution core sites covered by the side-scan sonar images, a total of 126 locations, are represented in Figure 3-27. This interpretation and discussion is not limited by the local image quality unlike the previous numerical regressions on digital number (DN50).

In general, low resolution cores whose principal fraction was silt were obtained from image areas classified as fine or finer sediments (88 percent of samples and areas matched). Similarly, cores whose principal fraction was classified as medium-sand were typically obtained from coarse or coarser sediment areas (86 percent of samples and areas matched). Fine-sands were found to be equally distributed between the fine and coarse sediment areas as might be expected given the limited classification types for the side-scan sonar interpretation. The few gravel samples were also split between fine and coarse areas which was not anticipated. However, this set of samples is believed to be too small and unrepresentative to infer any relationship between gravel and the side-scan sonar images.

The agreement between the three main sediment types by Laser analysis and the side-scan sonar images is considered to be quite good in that the descriptions and sample locations agree in the vast majority of cases. These results also indicate that the sediment types have remained the

same in the areas studied by the low resolution program. Given that the low resolution core sites were obtained throughout the area of side-scan sonar coverage, it is likely that the sediment area classifications have remained relatively constant during the Phase 2 study period (1992 to 1994).

Figure 3-28 presents a different perspective on the correspondence between the low resolution coring grain size results and the side-scan sonar data. This figure presents the DN50 values grouped by principal sediment fraction. This figure was constructed in the same fashion as the similar box- and-whisker plots presented in Section 3.2. The figure shows the steady increase in the DN50 value from silts to fine-sand to medium-sand plus gravel. Note that the fine-sand box-and-whisker plot straddles the range of DN50 from 40 to 60, which was the approximate range used to define fine- and coarse-grained sediment in the original side-scan sonar interpretations. This would explain the nearly equal distribution of fine-sand between the two sonar classifications seen in the previous figure (Figure 3-27). Note that this diagram is again limited to the 93 low resolution sites for which DN50 values could be defined.

Using the Tukey-Kramer honestly significant difference test, all three groups shown in Figure 3-28 were shown to be statistically significant and different from each other at the 95 percent confidence level. This is further confirmation of the correspondence between the side-scan sonar response and sediment type as classified by a standard technique.

The last figure to be presented under the discussion of grain-size distribution and side-scan sonar results is Figure 3-29. This figure shows the correspondence between the mean grain size on the phi scale and the DN50. Also shown is the relationship for the mean DN50 and mean phi for the confirmatory samples. This diagram and regression are nearly identical to the original diagram for the confirmatory samples presented in Chapter 4 of the DEIR (TAMS *et al.*, 1997) which is based on the median DN50 as opposed to the mean DN50. As is evident in the large diagram in Figure 3-29, the relationship between the mean DN50 and the mean diameter for the low resolution cores is not the same as that found previously. Nonetheless, both curves show a substantive decline in DN50 as the mean particle diameter decreases (phi increases). Although the regression curves are relatively close, the resulting low resolution regression yields a slightly better fit between DN50 and mean diameter after the exclusion of 4 points, based on a Mahalanobis analysis. The reason for the difference between the two curves is not known but it is likely that it is related to the

following issues. Specifically, the vast majority of low resolution core samples were obtained from fine-grained sediment areas and the data set probably does not contain a sufficient number of values to constrain the regression at higher DN and lower phi (larger diameters). In addition, as mentioned previously, the low resolution sediments were obtained from substantially lower depths in the sediment (0 to 9-inches for the low resolution top segment versus 0 to 2-inches for the confirmatory cores and less than 4 to 6-inches for confirmatory grab samples). The collection of deeper sediments may alter the underlying relationship. Lastly the conditions may have changed between 1992 and 1994, but this seems unlikely in light of the sediment classification evidence presented earlier.

In summary, the grain-size distribution data reaffirm the general conclusions concerning the use of the side-scan sonar data, which are:

- The side-scan sonar data can be used to classify large areas of the river bottom in terms of their sediment properties. This was confirmed by the samples collected which closely matched the sediment types identified by side-scan sonar.
- The acoustic signal as represented by the DN50 decreases as the sediment becomes more fine grained. This was confirmed by both the principal fraction correlation and the direct comparison of DN50 and mean diameter.

Comparison Between the Side-Scan Sonar Results and PCB Levels in Shallow Sediments

In the DEIR, a comparison was made between the DN10 and the 1984 NYSDEC sediment survey results. The comparison showed that the PCB levels in shallow sediments had a statistically significant inverse correlation with the DN10. The main limitation of the comparison was the length of time between the 1984 NYSDEC sediment survey and the 1992 side-scan sonar survey. As part of the analysis of the low resolution core results, the 1994 shallow sediment PCB levels were similarly compared to the 1992 side-scan sonar results eliminating much of the issue over time elapsed. In this instance, the DN50 was used instead of the DN10 since it has been the main parameter for comparison throughout this section. As shown in Figure 3-25, use of the DN50

relative to the DN10 does not appear to introduce any substantive error, given the inherent variability of these parameters.

In the original analysis in the DEIR, the DN values were grouped into bins of about five units (*e.g.*, DN10 of 40 to 45). The small bin intervals were usable for this analysis because of the large number of samples (about 1,200). The low resolution cores were far fewer in number (93) and thus would not support such narrow bins. For this reason, just three groupings of the total PCB data were made, based roughly on the important transitions seen in the original analysis using the 1984 data. These bins were defined as follows:

- DN50 greater than 60;
- DN50 less than or equal to 60 and greater than 30; and
- DN50 less than or equal to 30 and greater than 10.

No DN50 values were obtained lower than ten. The value of 60 corresponds to a marked change in the relationship between DN10 and the total PCB concentration in the original analysis. This value also represents an approximate sediment texture boundary based on the DN50 and the Laser grain size distribution for the confirmatory sediment samples.

The results for total PCB concentration in shallow sediments grouped by DN50 are shown in Figure 3-30. Evident in the figure is the marked increase in PCB concentration across the DN50 value of 60. A smaller increase occurs across the DN50 value of 30. When these bins were tested for statistical significance using the Tukey-Kramer honestly significant difference test, the first bin (DN50 greater than 60) was found to be statistically different from the other two bins. The latter two bins were not statistically different.

The results as presented in Figure 3-30 confirm the original findings of the DEIR concerning the acoustic signal as represented by the DN50. Essentially, coarse-grained sediments, typical of highly-reflective side-scan sonar areas (DN50 greater than 60) are distinctly less contaminated than the finer-grained, less-reflective areas. Based on the average or the median conditions, less-reflective finer-grained sediments are about ten to twenty times more contaminated than the coarser-grained areas. The results of the low resolution coring program in

fact yield a larger difference in PCB concentration across the DN50 threshold of 60 (about a seven-fold increase) than did the original analysis using 1984 data, although the change in this difference may not be statistically significant given the various uncertainties.

A similar comparison between low resolution core mass per unit area and DN50 was made using the same DN50 bins. The comparison is represented in Figure 3-31. The relationship covering the three DN50 groups in Figure 3-31 matches the results seen in Figure 3-30 almost exactly. This would be expected since so much of the PCB inventory is located in the shallow sediments as measured by the top core segments. The figure also reveals an approximate seven-fold increase in mean and median PCB inventory across the DN50 value of 60. This result implies that the side-scan sonar images can be used to estimate both shallow sediment PCB concentrations and sediment PCB inventories.

As a part of the DEIR, areas covered by the side-scan sonar images and interpreted as fine-grained sediments were considered to be areas of potentially high PCB contamination. This association was based on the interpretation of the 1984 sediment PCB data. The low resolution core data set supports this interpretation of the side-scan sonar images by again demonstrating a statistically significant correspondence between the image data and a more current sediment PCB inventory.

3.4 Summary of Chapter 3

This chapter has focused on the interpretation of the low resolution cores in the context of the conclusions from the high resolution cores presented in the DEIR (TAMS *et al.*, 1997). In this perspective, the results of the low resolution cores confirm the relationship between the changes in molecular weight relative to Aroclor 1242 (MW) and the molar ratio of the sum of BZ# 1, 4, 8, 10, and 19 to the total sample (MDPR). Confirmation of this relationship also confirms the occurrence of meta- and para-dechlorination and the absence of ortho-chlorine loss in the sediments. This represents an important confirmation since the low resolution cores can be considered more spatially representative of Upper Hudson conditions, thereby showing the consistency of the dechlorination process in the Upper Hudson. This confirmation also means that the MW term can be used as a surrogate for the estimation of mass loss by this process.

The low resolution cores yielded a similar average degree of dechlorination ($MW = 0.10$) to that obtained from the high resolution cores ($MW = 0.08$). Given that the low resolution core sites are focused on some of the most contaminated areas of the Upper Hudson and yet only an average mass loss of 12 percent ($MW = 0.10$) has occurred, it can be inferred that the rest of the Hudson has experienced an average mass loss of less than ten percent due to dechlorination, as was concluded from the high resolution cores.

The low resolution cores also showed that the degree of dechlorination in the sediments was proportional to the level of contamination. However, these results could only be shown to be consistent with the high resolution cores results and could not confirm the results due to factors inherent in the “vibra-coring” sample collection procedures and the sample homogenization process. Nonetheless, this consistency between programs is still an important result.

A close examination of the correlation between PCB concentration and the degree of dechlorination showed that the low resolution cores achieved an apparent degree of dechlorination equivalent to a high resolution sediment core at 3.5 times the low resolution core sample total PCB concentration. However, this 3.5-fold increase in response was attributed to the homogenization process wherein concentrated sediment layers would be mixed with low-level sediment layers, effectively lowering the measured concentration but leaving the degree of dechlorination in the concentrated layer intact. This was demonstrated by calculating this effect with the high resolution core results which yielded a similar shift in response.

Potentially cross-contaminated samples were ferreted out using the ^{137}Cs measurement at the core bottom and the PCB profile in the core to highlight those core segments most at risk for this problem. After screening the original 371 samples, 229 samples were kept to finalize the MW to total PCB relationship for the low resolution cores. Cross-contamination was an important issue in this chapter because of its differing effects on PCB mass and PCB ratios. The level of cross-contamination found in the cores will not represent a significant issue for the sediment-mass inventory estimates presented in the next chapter since the actual mass represented in the potentially cross-contaminated segments is so small.

The geometric mean total PCB concentration for the final data set of 229 samples was 30.8 mg/kg with a MW of 0.10 and an MDPR of 0.54.

A large number of ancillary parameters were examined for potential correlation with total PCBs, MW, and MDPR. Most parameters that could be related in some fashion to total organic carbon or silt content were found to exhibit some correlation with total PCB concentration. By and large, no strong correlations (*i.e.*, $|r| > 0.8$) were seen, although some were better than others. Among these, percent solids and bulk density had the strongest correlation coefficients ($R = -0.72$ and $R = -0.61$, respectively; Table 3-8) on log-transformed, length-averaged PCB concentrations.

Weak but anticipated relationships were also found with percent silt, median phi (ϕ), and principal sediment class when compared to individual PCB sample results on a log-transformed basis. Percent solids, solid specific weight and bulk density were the most highly correlated parameters for this comparison. Several individual grain-size parameters which represented the silt fraction of the sediment, specifically phi 4.5 to phi 6.5, exhibited the strongest correlations among the grain size parameters (0.41 to 0.47) and shallow sediment PCB levels. The TOC plus TKN data set was limited but yielded a weak correlation between total PCBs and both TOC and TKN across all depths. In addition, a weak but notable correlation was seen between the C/N ratio and MW. This suggests that maximum dechlorination occurs in wood-bearing layers, although a correlation between C/N and the visual presence of wood chips was not apparent (Section 2.3). Most likely, these layers represent highly concentrated, wood chip bearing sediments produced by the Fort Edward Dam removal in 1973 and the subsequent washout of the channel sediments in 1974 to 1976. Evidence of wood chips in Hudson River sediments was extensively noted by NYSDEC during the 1976-1978 surveys (Normandeau, 1977, Tofflemire and Quinn, 1979). In addition, Bopp *et al.*, 1985, noted the presence of high PCB concentrations and woody material in Hudson River sediments.

The radionuclide ^7Be was somewhat predictive, with ^7Be -bearing cores having statistically higher PCB levels than cores without ^7Be . Presumably the ^7Be marks areas of recent deposition while the absence of ^7Be indicates areas that are likely to experience scour and subsequent PCB loss. Surficial (0 to 1-inch) ^{137}Cs showed a stronger positive correlation ($r = 0.48$) with PCBs, although still not predictive. The fairly strong correlation between total PCBs and ^{137}Cs was

expected given the affinity of both analytes for fine-grained sediment and the thick low resolution core segments that served to integrate their different deposition histories. Shallow sediments correlated better than the core inventory (PCB/unit area) ($r = 0.34$), as might be expected since most of the PCBs, and probably most of the ^{137}Cs , was found in this layer.

^{137}Cs also correlated with MW, albeit weakly ($r = 0.36$). It is likely that the correlation between ^{137}Cs and MW is simply the result of each parameter's correlation with total PCBs. Similar weak correlations were found for many of the ancillary parameters. None had the level of correlation exhibited among the PCB parameters themselves.

The last part of the chapter explored the relationship between the side-scan sonar images expressed as a digital value (DN50) and the low resolution core results. The DN50 values showed similar correlations to the Laser grain-size distribution parameters for shallow sediment when compared to the confirmatory sediment samples originally used to interpret the side-scan sonar images. Most regression coefficients (r) for DN50 and the low resolution grain-size distribution parameters decreased relative to the confirmatory sample results. The weakened correlations were attributed a number of factors, with the confirmatory samples considered more representative of the surface sediments mapped by the side-scan sonar.

The strongest correlation for DN50 and grain-size distribution parameters were seen for mean phi (ϕ), median diameter ($d[50]$, and percent silt plus clay). The first two parameters both track the center of the grain-size distribution on a log basis inferring that the images are related to the general sediment texture as expected. Other diameter measures, near the center of the grain-size distribution (*e.g.*, $d(40)$ and $d(70)$) were similarly correlated with the DN50. The percent silt and clay tracked the proportion of fine-grained material and was inversely proportional to the DN50 as expected.

The classified side-scan sonar image areas (*e.g.*, fine sediment), were found to match the principal sediment fraction (*e.g.*, silt) very well for silt and medium-sand (85 percent accuracy or better). The samples classified with a principal fraction of fine-sand straddled the two side-scan sonar classifications of fine sediment and coarse sediment. However, this was consistent with the mapping approach since a DN50 value of about 50 to 60 was generally used as a boundary between

the two sonar classifications. This range of DN50 values also fell within the middle of the DN50 values for fine-sand so that splitting of the samples between the two classifications would be expected. Taken together, these results all confirmed the ability of the side-scan sonar images and interpretation to characterize sediments on a coarse/fine basis for the entire survey area.

A regression was performed on the DN50 and the mean phi as was done with the confirmatory samples in the DEIR. The low resolution core regression relationship was similar but not identical to the previous regression. This was attributed to two factors, the greater depth of the top low resolution core segments and the lesser number of low resolution core samples with relatively coarse sediments. Thus the low resolution core results were considered to be consistent with the previous work in this regard but could not be used to confirm the previously measured trend.

Lastly, the relation between DN50 and PCB concentration was examined. The prior examination completed for the DEIR showed higher PCB levels at low DN50 values. The results from the 1984 survey, as analyzed in the DEIR, showed a five- to ten-fold increase in total PCB concentration for sediments with DN50 less than 60 relative to those with DN50s greater than 60. The low resolution cores confirmed this result quite well with a seven-fold increase between the finer sediments ($DN50 < 60$) and the coarser sediment ($DN50 > 60$). A similar increase based on the DN50 threshold value of 60 was noted for the sediment PCB inventory as mass per unit area.

These results verify the usefulness of the side-scan sonar images for both the classification of sediment types as well as for the identification of areas of potentially high PCB contamination (greater than 50 ppm). In total, the low resolution coring results support conclusions of the previous Phase 2 investigations and interpretations. The correlations seen among the various low resolution core parameters are consistent with those seen earlier and affirm the application of the previous study conclusions to the entire Upper Hudson.

4. AN EXAMINATION OF HUDSON RIVER SEDIMENT PCB INVENTORIES: PAST AND PRESENT

A major goal of the low resolution sediment coring program was the estimation of sediment inventories in the areas of study. In this chapter, sediment inventories estimated from the low resolution cores are compared with historical studies of the sediments conducted by NYSDEC in 1976 to 1978 and 1984. In the TI Pool, low resolution cores results are compared on a point-by-point basis with the NYSDEC 1984 results. Below the TI Dam, low resolution core results are compared on a spatial basis with the 1976-1978 NYSDEC *hot spot* inventories. This chapter also contains a discussion of the near-shore sample results and compares them with the 1984 NYSDEC samples collected from the same region of the river. The last section of the chapter provides a summary of the analysis presented.

4.1 Sediment Inventories of the Thompson Island Pool

The TI Pool has been the subject of several large sediment surveys, each of which attempted to map sediment PCB inventories and areas of concentrated contamination. In 1976 to 1978, the first major survey of the TI Pool and the Upper Hudson was completed by NYSDEC. This survey was used to identify forty areas of highly contaminated sediments (*hot spots*), twenty of which were located in the TI Pool. In 1984, NYSDEC completed a second, more intensive survey of the TI Pool. On the basis of this survey, NYSDEC (Brown *et al.*, 1988) and Malcolm Pirnie (MPI, 1992) identified areas or polygons of elevated sediment contamination.

Because of the scale and coverage of the 1984 survey, it has been considered a benchmark in attempting to assess and understand sediment PCB inventories in the Upper Hudson. As a part of the Phase 2 investigation, the low resolution coring program was intended to assess the applicability of the 1984 survey to recent PCB inventories. This was to be accomplished by reoccupying selected 1984 sampling locations and collecting new cores to form a basis for comparison. As discussed in Chapter 2, the low resolution coring program was quite successful in reoccupying these sites. This section compares in detail the 1984 and 1994 surveys and discusses the ramifications.

PCB loss or gain from the sediment can take many forms. Scour, diffusion, groundwater advection, and biological activity can all potentially remove PCBs from a given location. Biological activity in the form of anaerobic microbial dechlorination can also serve to decrease PCB concentration in the sediments. PCB inventories can be increased chiefly by deposition, either with sediment contaminated by newly released PCBs or with redeposited sediments from other contaminated locations. Up until 1997 when GE brought nearly all PCB discharge from the Hudson Falls facility under control, it is likely that sediment deposition involved both fresh and redeposited material (General Electric Corp., 1991-1997). Tracing and estimating all of the various fluxes represent a daunting task made all the more difficult by inherent spatial and temporal variations. The low resolution coring program provided an alternate means of assessing these fluxes by using the PCB inventories found in the sediments to explain removal and deposition processes.

In the TI Pool, 63 sites originally sampled in 1984 were selected and reoccupied in 1994, providing a ten-year period of integration. The premise for analysis is then, has the sediment inventory of PCBs increased or decreased during the intervening ten years? While the premise itself is simple enough, there was concern that sediment heterogeneity, differing sedimentation rates, analytical technique differences, and other issues would confound the ability to discern true changes in the sediment inventory.

Concern over sediment heterogeneity factored directly into the low resolution site selections. Coring sites were selected in clusters of similar concentration and sediment texture in an attempt to minimize sediment heterogeneity of the sampling areas. Concern over differing sedimentation rates was addressed by individually assessing each core for completeness via the use of ^{137}Cs (Chapter 2). Analytical techniques were extensively reviewed to assess differences, as discussed below.

Before assessing changes in sediment inventory from 1984 to 1994, it was first necessary to establish a common measurement basis for comparison. Because of concern over differing deposition rates and variations in core segment intervals, cores were integrated over their lengths to yield mass per unit area (MPA) estimates as well as length-weighted averages (LWA).

The MPA was calculated as follows:

$$MPA \left(\frac{g}{m^2} \right) = \sum_{i=1}^n C_i \left(\frac{mg}{kg_{DW}} \right) * L_i \text{ cm} * SSW_i \left(\frac{g_{DW}}{cc} \right) * \frac{1kg}{1000g} * \frac{1g}{1000mg} * \left(100 \frac{cm}{m} \right)^2 \quad (4.1-1)$$

where C_i = the PCB concentration in the core segment in mg/kg dry weight (ppm)

L_i = the length of the core segment in cm

SSW_i = the mass of dry solids per unit wet core volume in $\frac{g - dryweight}{cc}$

n = number of core segments analyzed for PCBs

The LWA was calculated as follows:

$$LWA = \frac{\sum_{i=1}^m C_i * L_i}{\sum_{i=1}^m L_i} \quad (4.1-2)$$

where C_i and L_i are defined as above. The number of core segments in this calculation (m) may be the same or less than the total number of segments analyzed for PCBs (n) above. This distinction is made because LWA is most useful over the interval of recent sediments, rather than over the entire core length since a core may contain a considerable thickness of pre-1954 sediment. The selection of segments was based on each individual core profile. When the difference in PCB concentration between two adjacent segments was greater than an order of magnitude with the upper segment containing the higher concentration, the lower segment and all segments below it were excluded from the LWA.

Both parameters (MPA and LWA) can provide some insight concerning the change in sediment inventory from 1984 to 1994. The MPA provides the more intuitive interpretation. Its interpretation requires no knowledge of sediment depth so long as cores are considered complete or nearly complete. However, the inclusion of the solid specific weight (SSW) in the calculation adds another level of uncertainty to the parameter. Estimation of the solid specific weight for the 1984 survey was discussed extensively in the DEIR (TAMS *et al.*, 1997). The mean SSW value obtained for the low

resolution core segments in the TI Pool (1.09 g/cc) compares well with the mean value of the 1984 core segments (1.06 g/cc) but the comparison of the shallow (top-most) core segments shows a difference of about 10 percent (1.05 g/cc for 1994 vs 0.92 g/cc for 1984). This difference would yield a higher mass per unit area (by 10 percent) for the 1994 core given identical sediment concentrations. Lacking any basis on which to correct or select the SSW data means that this uncertainty must be incorporated into the MPA comparison.

The LWA concentration avoids this issue since SSW is not involved. However, the LWA adds a different uncertainty since core length has a direct bearing on its value. It is possible for two cores to have identical LWA but represent very different inventories simply on the basis of their length. Nonetheless, because of the general consistency of core lengths in both programs (roughly 15 to 30 inches), the length-weighted average provides an alternate basis for evaluating the change in sediment inventory. In the subsequent discussions, the MPA will be used primarily although information on LWA will also be provided.

Establishing a core integration scheme was only part of the basis needed to compare the 1984 and 1994 (Phase 2) survey results for PCBs. A second issue regarding analytical techniques had to be resolved before a direct comparison could be made. Specifically, analytical techniques for PCB quantitation had changed markedly both in congener resolution and on a sample reporting basis between 1984 and 1994. In particular, the 1984 data were quantitated and reported on an Aroclor, rather than congener-specific basis.

Three Aroclor results, representing Aroclors 1242, 1254, and 1260, were used in estimating the total PCB of the sample by their sample sum. (Brown *et al.*, 1988; TAMS *et al.*, 1997). The 1994 data were based on congener-specific standards, with no inherent tie to any Aroclor. Hence, the total PCB concentration by the Phase 2 method represents a true total.

As part of the Phase 2 investigation, a study was made of the differences between the two techniques. This is documented in Appendix E, which describes the quantitation issues relating the 1994 Phase 2 and 1984 NYSDEC PCB data. The recommendation of this analysis was to use the 1984 quantitation of total PCB as representative of the sum of congeners in the trichloro through decachloro homologue groups after applying the following corrections:

Trichloro to Decachloro homologues (mg/kg) = 0.934 x 1984 Total PCB Concentration (mg/kg)

(4.1-3)

During review of this analysis while preparing Appendix E, the correction factor was refined to 0.944. That value differs from the value actually used in the body of this report (0.934), but the one percent correction is minor and does not affect the comparison between 1984 and 1994 Thompson Island Pool inventories or the conclusions drawn from this comparison.

These results can then be compared with the same sum based on the low resolution core analyses. This interpretation of the 1984 PCB data also indicates that the 1984 analyses would have ignored the lightest congeners and so cannot yield any information on dechlorination. Both the trichloro to decachloro homologue sum and the total PCB value are used in the subsequent discussions. Emphasis is placed on the trichloro to decachloro homologue sum, however. From this point in the discussion, the trichloro to decachloro homologue sum is represented by Tri+.

Before beginning the analysis of the core data, it is useful to see the coring locations in the context of the river sediment classifications. Plate 4-1 is a key map to the locations of Plates 4-2 to 4-9. These plates consist of side-scan sonar images on which the river sediment properties have been mapped. In addition, each coring site is denoted along with the 1984 and 1994 MPA and LWA values. The 1984 values are located to the left of each core marker. The 1994 values are located to the right. Similarly, the LWA values are located above each marker and the MPA values are located below. Symbols for both the 1984 (solid circle) and 1994 (hollow circle) samples show the close agreement of the paired survey locations. The core symbols are also scaled according to the MPA value, providing a visual clue to the size of the inventory at a given location. The symbols also provide information on the extent of change at a location. The larger the difference in the circles, the greater the inventory change. The sediment classifications as derived from the side-scan sonar analysis are also shown on the map along the sedimentological boundaries. Evident in these figures are the general trends of mass loss at a majority of sites as well as the association of the greatest inventories in areas of fine-grained sediment.

A second set of plates provides more direct information concerning sediment inventory changes on a mass basis. Plate 4-10 is the key location map to Plates 4-11 to 4-19. These plates cover

the same areas as Plates 4-2 to 4-9 but they present only one circle per sampling site. This symbol is scaled to the absolute difference in total PCB inventory (MPA) between the 1984 and 1994 surveys. In addition, the percent change between the two surveys is given numerically at the upper right of each symbol. The percent change (Delta) was calculated for each coring site as follows:

$$\Delta = \left(\frac{MPA_{94} - MPA_{84}}{MPA_{84}} \right) * 100\% \quad (4.1-4)$$

Thus Delta is the absolute difference in total PCB inventory divided by the original 1984 inventory. Note that in Plates 4-2 to 4-19, all numbers for 1984 reflect the reported total PCB concentrations and were not corrected to Tri+ as discussed above. The corrected data will be presented and discussed later in this section.

Calculation of Delta requires a pair of NYSDEC and low resolution core results. Sixty-four of the 76 coring locations in the TI Pool had an associated NYSDEC core or grab. Four of these locations had grab samples which were only screened via a GC/MS technique which did not provide an absolute measure of contamination (see Brown, *et al.* 1988 and TAMS, *et al.*, 1997). An estimate of the level of contamination for these samples was assigned as part of the kriging analysis presented in TAMS, *et al.* (1997) but these values are not used here due to their large uncertainty. This left just sixty locations where it was possible to compare PCB quantitation directly. Of the sixty locations 45 were cores and 15 were grab samples.

In assessing sediment inventory changes, cores are preferable to grabs since the actual depth of a sediment sample is known. The depth associated with a grab sample is not well known. In addition, the grab samples were extrapolated to a depth beyond their expected penetration in an attempt to represent all PCB contamination at the location. This approach is generally acceptable when averaging large areas together to assess inventory on an average basis but it is not as useful on an individual sample basis. The lack of good depth control adds to the uncertainty associated with core to grab comparisons. Nonetheless, the core -grab pairs can still provide some useful information on the change in sediment inventory.

4.1.1 A Comparison of 1984 and 1994 Conditions

As a first step in assessing the difference between the 1984 and 1994 conditions, the individual core and core-grab pair profiles were compared. Appendix C contains diagrams for all low resolution cores collected in the TI Pool. Also shown on these diagrams are the profiles for the associated 1984 NYSDEC core or grab sample when available. Figure 4-1 contains several example profiles of cores from the TI Pool. In assessing the core profiles, the major concern was the change in sediment inventory from 1984 to 1994. Differences in slicing intervals between 1984 and 1994 were considered, so that the comparable thicknesses were compared. The sediment core classifications were not meant to be the final assessment on inventory change but were an attempt to examine the profiles in detail, rather than simply rely on the mathematical integration of the results. Cores were classified as to apparent inventory loss, represented by lower PCB concentrations as well as typically shallower contaminated profiles. Cores exhibiting inventory gain were characterized with higher sediment concentrations as well as deeper profiles. Some cores appeared to exhibit little change and were classified as such. Lastly, two cores were unclassified due to incomplete profiles. Table 4-1 is a list of the classified cores.

To a large degree, the interpretation of these cores was based on the profiles obtained during the high resolution coring work. Specifically, a core site undergoing steady deposition and burial would look similar to a high resolution core, allowing for thicker slices. This would be expected to generate the profile seen for core 5D in Figure 4-1. This can be compared to the high resolution core shape seen in Figure 4-2, representing core 19 collected near the TI Dam.

The reasons for the apparent changes in inventory between 1984 and 1994 were not always readily apparent. Sediment inventory losses could result from several processes as discussed previously. Sediment inventory gains presumably result from additional deposition at the coring site since 1984. Sediment heterogeneity, although minimized by the sampling site selection and collection process, was certainly a factor in yielding apparent changes in some cores. In a limited number of cores, however, there was enough information contained in the core profiles to definitively suggest sediment scour. In these instances, both the NYSDEC and the low resolution cores contained enough slicing intervals so as to indicate the depth of recent contamination at the time of collection. When the low resolution core had a substantively shallower recent sediment profile than the earlier NYSDEC

core, it was classified as exhibiting scour. The underlying assumption here is that the apparent upward movement in the sediment profile is the result of removal of the overlying layers by scour since it is unlikely that any other process could move PCB contamination from deeper layers and completely purge the deeper layers in the process. Of the 30 core sites where mass loss was evident, 8 profiles contained enough information to suggest scour as the mechanism for mass loss. Figure 4-3 shows a clear case of sediment scour at two of these sites. In both these cores, the absence of ^{137}Cs in the bottom-most layer provides the basis for the conclusion that no undetected PCBs remain below the 1992 core and thus that the sediment profile has become shorter over time, implicating scour as the removal mechanism.

After classifying the cores in this manner, the classifications were compared to the integrated core results as shown in Figure 4-4. This diagram represents the mass per unit area (MPA) estimates for total PCBs for the 1984 and 1994 site pairs. Sites with unchanged inventories would fall along the diagonal line through the center of the diagram. As can be seen in the figure, few points fall very close to the line. Note as well that the axes are log-scale. Nonetheless, also evident in the diagram is general agreement of the visual core classifications and the absolute core inventories. Core pairs showing loss fall below the line and vice versa, as expected. It is also apparent in this diagram, that the majority of points fall below the diagonal line, indicating a greater number of sites with inventory loss than gain. The discussions to follow will attempt to resolve the significance and cause of this trend.

Figure 4-5 contains a second representation of this data set. In the upper half of the figure, the 1984 and 1994 total PCB MPA values are graphed against each other. Also shown is the diagonal line mentioned previously as well as a regression line fit to the data. The data do not provide a linear representation but the trend is statistically significant and suggests that PCB inventory loss occurs more frequently at higher inventories. Also shown in Figure 4-5 is the MPA for just the trichloro and higher homologues (Tri+). In this instance, the 1984 trichloro and higher homologue concentrations are substantially higher than those for 1994, indicating extensive loss of those homologues from the sediment.

This loss becomes even more striking when the loss itself is plotted against the MPA for Tri+ for 1984. This is shown in the upper diagram of Figure 4-6. Evident in this plot is a linear relationship between Tri+ mass loss and the original Tri+ inventory. This should be contrasted

with the lower diagram in the figure which shows the relationship for the total PCB mass loss against the 1984 Tri+ inventory. The MPA for the Tri+ will be written as MPA_{3+} for the remainder of this section. These diagrams, as well as those of Figure 4-5, show that the total sediment inventory does appear to decline but not nearly in the manner seen for the Tri+ between 1984 and 1994. Part of the "goodness of fit" seen in the top diagram of Figure 4-6 stems from the presence of the Tri+ term in the variables on both axes. Thus, errors in Tri+ tend to be correlated and an overestimate of the degree of correlation is obtained. Nonetheless, there is a difference between the two diagrams in Figure 4-6. The MPA_{3+} loss consistently increases with increasing 1984 MPA_{3+} while total mass inventory (MPA) shows a less consistent trend, with many sites exhibiting inventory increases. This suggests that some of the loss seen in Figure 4-6 results from dechlorination, where the loss of Tri+ would not yield an extensive loss of mass. Rather this process serves to convert the congeners represented in the Tri+ to lighter congeners, specifically BZ# 1, 4, 8, 10, and 19. In this process, PCB moles are largely conserved while the PCB mass of the entire mixture can decline up to 26 percent. As was discussed in Chapter 3, no samples were found indicating PCB mass loss beyond 24 percent in the low resolution sediment cores based on the change in molecular weight relative to Aroclor 1242 (MW) (Figure 3-3). Thus the differences seen in the two diagrams represent the same processes in different ways. The plot of change in MPA_{3+} vs the 1984 MPA_{3+} tracks the combined effects of dechlorination and PCB loss to the overlying water column since both processes can lower the Tri+ inventory to essentially zero. The plot of change in total PCBs as MPA vs 1984 MPA_{3+} is much less sensitive to the dechlorination process since this process can only lower the total PCB inventory by 26 percent as opposed to loss to the water column which can potentially reduce the inventory to zero.

The difference in these processes and their effects on the sediment inventory can be seen more readily in log scale as shown in Figure 4-7. In the upper diagram, the loss in MPA_{3+} vs the 1984 MPA_{3+} is plotted. The diagram shows that the majority of Tri+ loss from the sediment is relatively minor in magnitude although nearly all samples exhibit some loss. This suggests that either no sediment PCB inventories have increased or else that increased inventories (presumably by deposition) were subsequently dechlorinated, resulting in no net increase in the Tri+ inventory. The latter scenario is supported by the lower diagram in Figure 4-7. This diagram shows the change in the total PCB inventory (MPA) vs the 1984 MPA_{3+} . In this diagram, both positive and negative inventory changes are

evident, indicating that some locations have seen gain despite their decrease in Tri+. Note as well that the level of gains are in some cases similar in scale to the larger losses.

Since PCB moles are largely conserved by dechlorination and lost by re-release to the water column, it should be possible to separate this process by tracking the PCBs on a molar basis. This requires an estimate of PCB molar inventory for both 1984 and 1994. The mole concentrations and moles per unit area can be calculated directly from the 1994 data set since it is congener specific. Calculation of the moles present in 1984 is a little less straightforward.

Knowing that the 1984 measurements represent the mass of Tri+, what is needed is an estimate of the mean molecular weight of this fraction at the time of sediment deposition to permit the calculation of the moles present at the time. This can be estimated in two ways. First, the mean molecular weight of the Tri+ fraction can be obtained from Aroclor 1242 directly since the congener composition of Aroclor 1242 was measured as part of the Phase 2 investigation. Based on this analysis, a mean molecular weight of 275 grams per mole (g/mole) is obtained for the Tri+ fraction. Alternatively, this value can be estimated from the recently deposited sediments of the high resolution cores. Figure 4-8 shows the relationship between the mean molecular weight for the Tri+ fraction and the MW of the sample for the entire set of Upper Hudson high resolution core samples. Also plotted on the diagram are the results for the low resolution cores, although these are not used in the regression. Given that dechlorination is restricted to the sediments, it is likely that depositing sediment will be similar to Aroclor 1242 in molecular weight since this was the major form of PCB released. That water column contamination was derived from Aroclor 1242 or its altered form in the sediments was demonstrated in the DEIR (TAMS, *et al.*, 1997). In fact, because of the nature of PCB partitioning, suspended matter appears more Aroclor 1242-like than the associated whole water sample, even when the water column load is highly altered. Thus extrapolating the trend of molecular weight for Tri+ vs MW back to a value for MW of zero yields an alternate estimate for the molecular weight at the time of deposition. As shown in Figure 4-8, a regression line through the high resolution core data yields a value of 281 g/mole for the molecular weight at a MW of zero. Alternatively, the high resolution core data themselves appear to cross the MW value of zero at roughly 282 to 285 g/mole, providing a third estimate. Note in the diagram that few samples exceed the value of 285 g/mole, suggesting this may be close to the actual molecular weight at time of deposition. The range of molecular weights based on these three values is 275 to 285 g/mole, or less

than a 4 percent range. Thus the choice of any of these will have little effect on the mole estimates. The value obtained from the zero intercept of the curve in Figure 4-8, *i.e.*, 281 g/mole was used as the molecular weight estimate for Tri+ at the time of deposition.

Having a molecular weight estimate for the PCBs in sediments in 1984, the change in mole content of the sediments can be calculated using a few additional assumptions. Since the 1984 measurements best describe the Tri+ inventory, no additional data are available to define the concentration of lighter congeners. Changes in moles between 1984 and 1994 must then be constrained to only the PCB molecules measured in 1984, *i.e.*, the trichloro and higher homologues. However, in 1994, not all of the molecules present as trichloro and higher homologues will still be in their original form. Many will have been dechlorinated during their residence in the sediments and converted to the congeners BZ#1,4,8,10 and 19. Thus to completely account for the original Tri+ molecules, the 1994 mole tally must include the current inventory of Tri+ as well as the dechlorination product congeners. However, the occurrence of lighter congeners in the sediment in 1984 would also be included in the mole tally for 1994 if the congeners are still present in the sediment at the time of low resolution core collection. Since no information is available to constrain the estimate of lighter congeners, their contribution to the current sediment inventory cannot be calculated and will be assumed to be zero. This clearly represents an underestimation but it will serve to provide a minimum estimate or lower bound on the number of moles lost from the sediment between the 1984 and 1994 sediment surveys.

It should be noted here that the Tri+ sum for the 1994 sediment samples represents all trichloro and higher congeners excluding BZ#19. This was done to separate the dechlorination products from those potentially alterable. This difference could not be made for the 1984 sediments since no congener specific data were available. This represents a minor error if the sediments were unaltered since BZ#19 is less than a few percent in Aroclor 1242. If the sediments were extensively altered, this error simply becomes part of the larger uncertainty associated with the assumption that no lighter congeners were present. In any event, the result is still a minimum estimate for the moles lost.

The range of mole loss and the range of loss in Tri+ as MPA₃₊ loss in moles is represented in Figure 4-9. This figure shows the definitive loss in the Tri+ relative to the mole differences which are centered more closely to zero. When the 60 low resolution core/1984 core and grab pairs were

considered as a whole, the distribution for the mass change was found to be statistically different from zero while the molar change was not. This figure again demonstrates that loss in $\Sigma\text{Tri}+$ does not directly correspond to loss in PCB moles.

These results are presented graphically on Plate 4-20 as well. This plate is a map of the TI Pool showing the coring locations considered in this analysis. At each matched coring location, a circle is plotted whose diameter is proportional to the change in the $\Sigma\text{Tri}+$ mass due solely to molar loss or gain. Red circles indicate loss while black circles indicate gain. Losses represented on this map are exclusive of dechlorination and instead represent sites exhibiting mass loss to the overlying water column via one or more transport mechanisms. Gains are presumably due to post-1984 deposition. The distribution of red and black circles on Plate 4-20 show some areas to be experiencing consistent losses (*e.g. hot spots 10 and 16*), others gains (*e.g. northern end of hot spot 8*) while most exhibit a mixture of losses and gains. Overall there are more locations exhibiting loss than gain. The next section of this report examines the relationships within the data to aid in the understanding of the distribution of losses and gains seen in Plate 4-20.

4.1.2 Assessment of Sediment Inventory Change Based on the Original 1984 $\Sigma\text{Tri}+$ Sediment Inventory

With the measures of sediment inventory (MPA and MPA_{3+}) and the estimates of molar content, it is possible to assess the changes in the sediment inventories due to PCB loss or gain from the water column as well as to dechlorination. The goal of the analysis presented here is to find useful groupings of the data which can provide a basis for applying the low resolution core results to larger areas of the TI Pool. As a first step, the PCB mass and PCB molar differences were compared statistically. The results were grouped based on the 1984 $\Sigma\text{Tri}+$ sediment inventories (MPA_{3+}). Specifically, the data were grouped into cores from areas less than 10 g/m^2 and greater than 10 g/m^2 . There were too few samples in the lower concentrations to further subdivide the groups without losing much of the statistical power of the tests. The selection of this split point was based on the regression line shown in Figure 4-5 which crosses the diagonal near this value. A value of 10 g/m^2 is generally characteristic of the more contaminated sediments of the Upper Hudson. The length-weighted average concentration corresponding to 10 g/m^2 is approximately 12 mg/kg . Peak concentrations for these cores are 50 mg/kg . Thus the greater-than- 10-g/m^2 group corresponds to sediments typically found in hot

spot areas. To assess these differences, the results were compared on both the absolute difference in inventory as well as a relative difference. The relative difference for MPA was calculated as follows:

$$\Delta_{PCB} = \frac{1994 \text{ MPA} - 1984 \text{ MPA}_{3+}}{1984 \text{ MPA}_{3+}} \quad (4.1-5)$$

where: Δ_{PCB} is the relative or fractional change in mass per unit area (Δ_{PCB})

1994 MPA is the total PCB mass per unit area, for 1994 results; and

1984 MPA_{3+} is the Tri+ mass per unit area for 1984 results.

The relative difference for the molar inventory was similarly calculated as:

$$\Delta_m = \frac{\frac{1994 \text{ Total Moles}}{m^2} - \frac{1984 \Sigma \text{Tri} + \text{Moles}}{m^2}}{\frac{1984 \Sigma \text{Tri} + \text{Moles}}{m^2}} \quad (4.1-6)$$

where: Δ_m is the relative or fractional change in moles per unit area (Δ_m)

1994 Total Moles/ m^2 is the molar sum of the trichloro and higher homologues plus the moles of BZ# 1, 4, 8, 10, and 19 on a unit area basis; and

1984 Tri+ moles/ m^2 is the molar sum of the trichloro and higher homologues on a unit area basis.

The delta function is not a normally distributed one as can be seen in the first diagram in Figure 4-10. Specifically, the loss range is between 0 and 1 while the gain can range to infinity. The log-transform of this data helps to remove some of the skew but it is still not normal. Since a log-transform of a negative number is not defined, a value of 2 was added to all Delta results before performing the log transform. Although the log-transformed data are still not normal, the distribution is sufficiently close to normal to permit the use of parametric tests to assess change. Non-parametric tests will be used to confirm the statistical significance determined from the parametric tests.

The first analysis presented for the $>10 \text{ g/m}^2$, $<10 \text{ g/m}^2$ MPA data grouping is shown in Figure 4-11. This figure shows the distributions for the absolute difference in molar inventory for the two groups. Declines in this inventory represent molecular loss from the sediment, indicating PCB release from the sediment to the overlying water, or could result from destruction of PCBs. Increases suggest additional deposition of PCB-bearing sediments. Evident in the figure is the extensive overlap between the two groups. This overlap is confirmed by the Tukey-Kramer circles shown on the right of

the figure. Statistically significant differences between groups are indicated when the circles are separate or touch only slightly. In this instance, the circles indicate that these groups are not significantly different for the molar inventory change. This analysis indicates no trend in absolute molar inventory change with 1984 PCB sediment inventory. Further explanation of the Tukey-Kramer circles can be found in the key sheets to Appendix F. A definition of the Tukey Kramer honestly significant difference (HSD) on which these circles are based is given in the glossary.

In Figure 4-12, the absolute mass change is examined as a function of these two groups. Again the groups show substantive overlap which is confirmed by the Tukey-Kramer circles. This analysis also indicates the absence of a trend in absolute mass difference with 1984 PCB sediment inventory. It should be noted in the data represented in both Figure 4-11 and 4-12 that, although the two groups were not statistically different from each other, the $>10 \text{ g/m}^2$ was statistically less than zero, confirming the occurrence of net PCB loss from the sediment for this group.

Examining the differences in PCB inventory on an absolute basis was not particularly fruitful, in part because the magnitude of the PCB change can represent both analytical variability as well as real change. By examining the relative changes in inventory using the delta functions described above, much of the analytical variability can be diminished in importance relative to real change since analytical variability is typically small relative to the absolute measurement values. Figure 4-13 presents the analysis for the relative change in molar inventory (Δ_M) as a function of the two inventory groups. Note that the results are based on the function:

$$\log(\Delta_M + 2)$$

since the log of values less than or equal to zero is undefined. In this analysis, the groups are found to be statistically different, with sediments $>10 \text{ g/m}^2$ exhibiting a large relative loss of approximately 28 percent.

This result indicates that on average, higher concentration sediments have shown a substantive, statistically significant loss which cannot be accounted for by dechlorination. While the mechanism(s) responsible for this loss are not known, some cores clearly suggest scour as a possible loss mechanism. Other transport processes may also be important, such as preferential flux from the

sediments to water column of monochlorobiphenyl and dichlorobiphenyl dechlorination products, as suggested by the seasonal PCB release patterns noted in recent GE water column data. Most importantly, though is the clear loss of PCB molecules from sediments of higher inventories, presumably to the water column. This result confirms the findings of the DEIR wherein water column PCB contamination was shown to originate within the TI Pool. The analysis presented documents a likely candidate for this source, *i.e.*, the sediments of relatively higher contamination. This is not to suggest that all Upper Hudson water column contamination is associated with the TI Pool sediments. As will be shown later in this report, sediments below the TI Dam also show PCB loss. This is also consistent with the DEIR which indicated the presence of additional PCB input to the water column downstream of the TI Dam during a spring sampling event (Transect 3) and possibly during summer sampling as well.

This analysis also indicated the occurrence of a net inventory gain for the sediments less than 10 g/m². In this instance the average gain was 104 percent, representing a potential doubling of the sediment inventory. However, this gain must be considered in light of the way it was derived. Specifically, the estimate of the 1984 molar inventory represents a lower bound estimate for the inventory due to the fact that no information was available concerning the lighter congeners (*i.e.*, monos and dis). This premise serves to minimize any molar loss estimated between 1984 and 1994. Thus statistically significant losses have a high probability of being true and in fact larger than estimated. However, gains have the opposite concern. Because the 1984 estimate is a lower bound, an apparent gain would be expected based on undercounting of monochloro- and dichlorohomologues. Therefore, statistically significant gains may be much less than estimated and have the potential not to be real. Thus from the analysis presented above, it can be concluded that definitive PCB losses have occurred for sediments greater than 10 g/m² to a degree greater than that estimated here, presumably via loss to the overlying water column. In addition, the data suggest inventory increases for sediments less than 10 g/m², although to a degree less than that estimated here.

As a final part of the analysis presented here, two non-parametric tests were conducted to confirm these findings. Specifically, a rank sums test and a median test were performed on these data. These results confirmed the statistically significant difference between the two data groups at a greater than 99 percent probability. These results are included along with the rest of the statistics for this analysis in Appendix F.

The next analysis examined the relative change in sediment mass (Δ_{PCB}) and is shown in Figure 4-14. Note that the results are again based on the function:

$$\log(\Delta_{\text{PCB}} + 2)$$

since the log of values less than or equal to zero is undefined. This analysis also indicated a statistically significant decline in sediment inventory for sediments greater than 10 g/m². In this instance the decrease was estimated to be 39 percent. The decrease in mass per unit area for these sediments represents the sum of both the dechlorination loss and the loss to the overlying water column. In fact, this loss is quite consistent with the other independent determinations of loss. Specifically, the previous analysis of molar change suggested an inventory decrease of 28 percent via loss to the water column. Assuming that all molecules are equally likely to be lost as would be the case in a scour scenario, this 28 percent molar loss translates to a 28 percent mass loss. In the discussions in Chapter 3, a mean dechlorination loss of 12 percent was found for sediments of the Upper Hudson based on the change in molecular weight (MW). These two processes yield an approximate mass loss of 40 percent which compares closely with the direct measure of mass loss estimated here.

The Δ_{PCB} also yielded an inventory gain for sediments less than 10 g/m². This was estimated to be 87 percent. Like the molar inventory gain, however, this estimate represents an upper bound on the actual inventory gain. These results were confirmed using the non-parametric tests mentioned previously, which yielded a greater than 99 percent probability for significant difference between the groups. The test results are contained in Appendix F.

The 1984 grab samples were examined as an additional sub-grouping of the MPA groups (Figure 4-15) to evaluate the accuracy of the grab samples relative to the cores in regard to sediment inventory. The grab samples appear to yield potentially lower values for Δ_{M} but no statistical difference was found. To some degree this analysis is limited by the number of grab samples available (15).

4.1.3 Assessment of Other Potentially Important Characteristics

Two other properties were used as criteria to group the Delta values and look for statistically significant relationships. Specifically ^7Be and a cohesive/noncohesive sediment properties were used to group the sediments. The ^7Be results from the surficial core layer (0 - 1 in.) were used on a presence/absence basis to group the Delta data. This yielded two statistically significant groups, with the ^7Be absent group yielding a lower value for Δ_{M} . This may indicate that the absence of ^7Be is a relatively good indicator for sediment PCB loss, presumably to the water column. This is a somewhat different result than that found for sediments below the TI Dam as discussed in the next section. Part of this difference probably results from the lack of one-to-one sample correspondence between the earlier and current study for samples collected below the TI Dam. A statistical summary sheet is provided in Appendix F for this analysis.

The data were also grouped based on a cohesive/noncohesive sediment classification developed by Limno-Tech and reported in the Preliminary Model Calibration Report (LTI, 1996). This classification was largely based on the side-scan sonar results. In this analysis, a general trend toward higher inventory losses was seen for cohesive relative to noncohesive sediment but it was only significant at the 90 percent confidence level. Statistical summary sheets are provided in Appendix F for both the ^7Be and cohesive/noncohesive analyses.

4.1.4 Implications of the Inventory Assessment

The implications of the inventory changes noted above are important in assessing the current status of the TI Pool sediments. Specifically, the inventory losses represented by Δ_{M} are presumed to apply to all similar sediments. This implies that most hot spots within the TI Pool have undergone substantive losses to the water column via scour or some other release mechanism. The estimate for the degree of mass loss via this process is 28 percent although this is a lower bound estimate. Given that the inventory for these hot spots is on the scale of ten or more metric tons, this mass loss is consistent with some of the recent estimates of release to the water column of 0.5 to 1 kg/day. Over ten years, this water column load would represent 1825 to 3650 kg. This is not to imply that there have been no additions to the PCB inventory of the TI Pool. As noted in the DEIR, upstream releases may have served to add PCBs to the TI Pool sediments. The point here is to denote that, nonetheless,

sediment inventories from the more contaminated areas have declined consistent with a sediment release process. Again dechlorination, while present, is limited in its ability to cause PCB inventory decline and is clearly overshadowed by the scale of the sediment PCB losses to the water column. Figure 4-16 shows the distribution of the nearly the entire set of PCB mass/area samples for the trichloro and higher homologues, based on the 1984 survey. Roughly one third of these samples represent sediments which would be expected to see this level of PCB loss.

The inventory assessment also yielded an upper bound on the expected gain that might be seen for the low level ($<10 \text{ g/m}^2$) sediment. While some of the inventory gain would be expected to result from the upstream releases from the GE facilities, it also is probable that some portion of the gain in low-level sediment is from the redistribution of PCBs from more heavily contaminated areas.

4.2 Sediment Inventories of the Upper Hudson Below the Thompson Island Dam

As part of the low resolution coring program, six *hot spots* below the TI Dam were selected to be surveyed with some additional coring in a limited number of areas. During sampling the field crew unintentionally extended the coverage around *Hot Spot* 34 to include *Hot Spot* 35, bringing the number of *hot spots* covered to seven. These *hot spots* were originally chosen since they represented the majority of *hot spot* contamination (74 percent) below the TI Dam (Tofflemire and Quinn, 1979). Table 4-2 provides summary information on these *hot spots*.

The original premise for the low resolution coring program below the TI Dam was to provide independent estimates of sediment inventories in a number of *hot spot* areas to establish current conditions and to compare with the 1976-1978 NYSDEC survey. Some additional coring was also planned to explore other areas of potential contamination. To meet these objectives, 5 to 14 cores were placed within each of the six main *hot spots* as well as several just beyond each *hot spot* boundary. The cores within each *hot spot* area were averaged to obtain an estimate of the concentration in mass per unit area for the *hot spot*. The coring locations outside the *hot spot* boundary were used to confirm the boundary itself. Cores placed outside the boundary were expected to yield substantially lower concentrations per unit area. Additional exploratory cores were placed in *Hot Spot* 35 (4 cores) as well as in three additional study areas.

Plates 4-21 to 4-28 show the locations of the *hot spots* surveyed by the low resolution coring program, the original 1976-1978 NYSDEC sampling sites, and the sediment classifications developed from the side-scan sonar for the areas covered. Plate 4-29 is a key to the locations of Plates 4-21 to 4-28. Original side-scan sonar images for these locations were presented in Plates 3-11 to 3-20. Plates 4-21 to 4-28 also provide the LWA concentrations for shallow sediments at 0 to 12-inches for both surveys. The location markers are coded to indicate ⁷Be absence or presence for the 1994 low resolution core survey and to indicate a core or grab sample for the 1976-1978 NYSDEC survey.

4.2.1 Calculation of the Length-Weighted Average Concentration (LWA) and Mass Per Unit Area (MPA) for Sediment Samples Below the TI Dam

Before estimating current sediment inventories or comparing previous and current conditions, it is first necessary to establish a consistent measurement basis for sediment PCB contamination. The issues here are similar to those raised for the 1984 to 1994 survey comparisons discussed in Section 4.1. While estimation of current inventories can be done in a similar fashion to the TI Pool cores, the comparison to the previous studies requires resolution of analytical techniques and sampling procedures between the 1994 low resolution core survey and the 1976-1978 NYSDEC survey.

The 1976-1978 sampling program results were examined by a number of investigators who translated the results into area estimates and inventories (Tofflemire and Quinn, 1979; MPI, 1978; Brown *et al.*, 1988; and MPI, 1992). In particular, the 1992 study by Malcolm Pirnie, Inc. established sediment inventories for a series of potential dredge areas as part of a study undertaken for NYSDEC. This study was never finalized but a draft report was made available to the USEPA. The data organization and presentations in the 1992 MPI report were used extensively in this report, as were the original *hot spot* estimates made by Tofflemire and Quinn, (1979) and MPI (1978).

Analytically, the 1994 and 1976-1978 sampling programs are based on different procedures. The low resolution core survey PCB analyses were based on congener-specific capillary column gas chromatography. The 1976-1978 NYSDEC survey in contrast used packed column gas chromatography with Aroclor-based standards, representing Aroclors 1221, 1016, and 1254. These Aroclor mixtures have relatively few common congeners among them so “double-counting” of

congener concentrations is unlikely. The simple sum of the reported Aroclor values yields an estimate for total PCB concentration, which is probably the best that can be done to create a value for comparison to the low resolution coring results. Although this sum is a best estimate for total PCBs, the estimate is still limited in its quantitation of the lightest congeners. Specifically BZ #1 and #4 were not directly quantitated and may have been present at elevated levels relative to Aroclor 1221 due to dechlorination processes. Thus, the sum of Aroclors may represent a lower bound on the actual PCB concentration in the sediments in 1976-1978.

Sampling techniques were also different between the 1976-1978 and 1994 surveys. In 1976 to 1978 both core and grab samples were collected by NYSDEC. Cores were typically 12 to 16-inches in depth and subdivided into two to three segments for analysis. Most PCB contamination (greater than 80 percent) was found within the top 12-inches (MPI, 1992). Grab samples were assumed to penetrate to about 4-inches (Tofflemire and Quinn, 1979; MPI, 1992). In calculating sediment inventories, core results were simply integrated by length. Grab sample results were extrapolated to 12-inches, based on a factor developed from the coring results. The factor for the grab samples was developed by Malcolm Pirnie, Inc. (MPI, 1992) for NYSDEC based on the ratio of surface sediment PCB levels (0 to 4-inches) to those of the entire core.

To calculate the sediment PCB inventory and to compare 1976-1978 conditions with those in 1994, PCB results from both programs were reduced to LWA and MPA values. The calculation of the LWA values was relatively straightforward since most cores were analyzed to a depth of at least 12-inches and the grab sample data had already been corrected to this depth by MPI. LWA was generated for shallow sediments, at 0 to 12-inches deep, for both 1976-1978 and 1994 data sets. For the 1994 data when the top-most segment ended above the 12-inch mark (*e.g.*, a nine-inch top segment), the remaining inches were included in an LWA by using the concentration of the next deepest layer for just the needed inches. When the top-most segment was greater than or equal to 12-inches, the reported concentration for the segment was used without modification. Length-weighted averages for 0 to 12-inches were previously determined by Malcolm Pirnie, Inc. (MPI, 1992) for the 1976-1978 core and grab samples, as mentioned previously. Due to discrepancies between the values reported by MPI and those contained in the electronic NYSDEC database, the results could not be cross-checked. As a result, the MPI results, which were already in the desired form, were used in this report.

Determination of the MPA for the 1976-1978 data set was more problematic due to the lack of density data for this study. Although it is never explicitly stated in the original report by Tofflemire and Quinn (1979) nor in the analytical report by O'Brien and Gere (1978), it can be inferred from the way the data are used that the original PCB analyses were reported on a dry-weight of sediment basis. Therefore, to calculate the PCB mass per unit area from these results, the solid specific weight (weight of dry sediments per unit volume of wet sediments) is required. Since this is an essential part of the calculation, estimated values for the solid specific weight (SSW) were obtained based on the strong correlation between total PCBs and SSW for the low resolution coring program as shown in Figure 3-15. When this plot is reversed by using the total PCBs for the grouping (bin) values, the median and mean SSW values for each PCB range can be obtained from the relationship as shown in Figure 4-17. Utilizing the 1976-1978 total PCB concentrations, SSW values were obtained for the NYSDEC core and grab samples based on the bin mean values listed in Table 4-3. With this parameter, the MPA values for the 1976-1978 sampling locations could be calculated by the formula described in Section 4.1. Note this correction for SSW represents a potentially large (20 to 50 percent) correction to the original MPA estimates generated by MPI (1992) and Tofflemire and Quinn (1979). Specifically, the earlier estimates assumed a SSW of 1 g/cc for all sediments. In light of the current low resolution coring work, this assumption was found to be an oversimplification. At the PCB levels reported by MPI (1992), SSW ranged from 0.5 to 0.79 g/cc with the lowest SSW values at the highest concentration. When using a constant SSW of unity, the contributions by the most contaminated sediments will be overestimated. For the discussions on MPA which follow, the 1976-1978 MPA values have been calculated using the low resolution core SSW to PCB concentration relationship given in Table 4-3. These results will be contrasted against the original MPI (1992) and Tofflemire and Quinn (1979) estimates under the discussion of *hot spot* PCB mass later in this section.

The 1976-1978 PCB results in the TAMS database and in this report were obtained directly from NYSDEC (Bopp, 1990), as well as from the MPI (1992) report. In particular, the extrapolated grab sample results and the length-weighted average core values were taken directly from the MPI report. Visual sediment classification data and grain-size distribution data were obtained electronically from NYSDEC as well as from Normandeau (1977).

4.2.2 Comparison of 1976-1978 Sediment Classifications and the Side-Scan Sonar Interpretation

Before beginning the discussion of PCB inventories for 1994 and 1976-1978 data sets, it is useful to establish the comparability of the sediment classification data available for the two data sets. A good level of agreement between the 1976-1978 and 1994 Phase 2 conditions serves to support the use of the historical data set as a good characterization of the river, as well as to further confirm the internal consistency of the various sediment classification data sets. Consistency between 1976-1978 sediment classification data and the current conditions would also imply that river-bottom conditions have remained relatively constant over time, that is, areas with fine-grained sediment tend to remain fine-grained and coarse-grained sediments tend to remain coarse-grained. This comparison was made by contrasting the principal fraction classifications used by NYSDEC and its consultants for the 1976-1978 samples with the classification developed from the side-scan sonar images. This is similar to the analysis presented in Chapter 3 for the low resolution core grain-size distribution data and the side-scan sonar classifications. However, consistency in sediment classification cannot be used to infer that the sediments do not move or that their PCB inventories are unchanged. As was discussed in Section 4.1 and presented below, PCB inventories have substantively changed in many instances.

Sediment classification data were obtained for a total of 493 locations throughout the area of side-scan sonar coverage. These locations were obtained for both the TI Pool and for areas below the TI Dam. The sediment classification data for the 1976-1978 survey was obtained from two sources: a report by Normandeau Associates, Inc. (1977) and an electronic data file transmitted to the USEPA (Bopp, 1990). The data from the Normandeau report represented standard grain-size distribution data reported on a phi scale plus silt and clay fractions. The data from both sources were converted to a principal fraction by summing across phi bins as shown in Table 4-4. The largest percent fraction among the classifications developed for each sample, *i.e.*, coarse-sand, medium sand, fine-sand, silt, and clay, was defined as the principal fraction. Of the 405 samples reported by Normandeau (1977), 278 were located within the areas covered by side-scan sonar.

Data for other locations were contained in the electronic data files obtained from NYSDEC. These data contained a numerical code describing the sediment texture. The original sediment

description for these codes was contained in Tofflemire and Quinn (1979). These codes were used to assign the principal fraction classification as shown in Table 4-5. Using this translation, the electronic files provided an additional 215 locations within the side-scan sonar coverage, bringing the total number of 1976-1978 survey locations to 493. A new sediment classification, “muck”, was used for the description data set only. The precise sedimentological classification for these “muck” samples is not known, but they are believed to represent organic-rich silts and fine-sands.

The comparison between the NYSDEC classifications and those by side-scan sonar interpretation is given in Figure 4-18. This figure shows the sample data organized by NYSDEC principal fraction and side-scan sonar classification. The primary sediment category collected during the 1976-1978 survey was fine-sand. The agreement between the NYSDEC and side-scan sonar classification appears quite good. Beginning with the silt and muck classifications, it is apparent that the majority of the silt and muck samples were obtained from areas classified as fine-grained. Similarly, medium-sand and coarse-sand samples by the NYSDEC survey were generally mapped to coarse-grained sediments by the side-scan sonar interpretation. As a group, medium-sand and coarse-sand samples were mapped as coarse sediments roughly 72 percent of the time. For silt and muck, the agreement was also good but not as accurate, with about 57 percent of the samples mapping as fine-grained sediment.

All NYSDEC sediment classifications except for clay had a small but non-trivial number of sites which were mapped as rocky locations by the side-scan sonar. These sites are attributed to pockets of sediment located in and among the rocks or rocky outcrops on the river bottom. Although rocks would be the most prevalent kind of material in these areas, the standard sampling procedures used by NYSDEC (*i.e.*, coring tubes and relatively small grab samplers) would not reflect this. Instead, these samplers would focus on the coarse-sands to fine sediments found among the rocks which are more readily collected by these samplers. Thus, rocky areas yield a variety of sample types. When rocky areas are excluded from the tally, the fine-grained fractions of silt and muck yield a 66 percent rate of agreement with side-scan sonar. Similarly, the coarser fractions, medium- sand and coarse-sand as classified by NYSDEC, yield an improved agreement of 83 percent when the rocky locations are excluded.

Only seven NYSDEC sampling locations were classified as clay, yielding a very small group to assess. Nonetheless, only two of the seven samples were obtained from fine-grained sediment areas as defined by the side-scan sonar. The reason for this is unclear but may represent small pockets of glacial lake clays located in among coarse-grained sediment areas. During the Phase 2 confirmatory sampling, all clay samples collected were associated with historical glacial lake deposits.

Fine-sands yielded the greatest number of samples in the NYSDEC data set. The results map out as approximately 55 percent coarse-grained sediment and 45 percent fine-grained sediment based on the side-scan sonar, when rocky locations and the other minor areas are excluded. This split in area type is very consistent with the results obtained for the low resolution cores, as shown in Figure 3-28. Note that Figure 3-28 uses bins based on the side-scan sonar assignments and maps the grain-size classification whereas Figure 4-18 uses bins based on the NYSDEC classifications and maps the side-scan sonar assignments. Fine-sand samples are approximately evenly split (52 percent coarse-grained and 48 percent fine-grained) using the side-scan sonar classification and the NYSDEC results (upper diagram of Figure 3-28). These results are consistent with the resolution afforded by the side-scan sonar images, in that the acoustic signal (DN50) value used to separate fine-grained and coarse-grained sediments (55 to 60) roughly corresponds to the middle of the range of DN50 values obtained for fine-sands, as shown in Figure 3-30. Thus an even split of fine-sand samples among fine-grained and coarse-grained sediment areas would be expected for both the low resolution core sites and the NYSDEC sampling locations.

Although the rates of agreement between the NYSDEC classification and the side-scan sonar classifications are not as good as that for the low resolution core samples, the agreement is still considered acceptable. The poorer agreement is due in part to the use of visual classifications, as well as standard grain-size distribution analysis in this comparison. There is also the possibility of changes in sediment type in a limited number of cases. Overall, the historical 1976-1978 NYSDEC grain-size distribution results appear quite consistent with the current Phase 2 side-scan sonar classifications and the Phase 2 sediment grain-size distribution results. Historical silt, fine-sand, and medium-to-coarse-sand samples all map onto the side-scan sonar classifications in a manner consistent with the low resolution core data. This result supports the contention that Hudson sediment classifications have remained relatively constant over the last 15 years for large areas of the river bottom. That is, large areas of fine-grained sediments as classified in 1976-1978 are still areas of

fine-grained sediments. Similarly, large areas of coarse-grained sediments also remain as originally classified. However, these results cannot be used to imply that the PCB inventories remain intact. The status of the PCB inventories below the TI Dam is discussed in the next section.

4.2.3 Comparison of Sediment PCB Inventories: NYSDEC 1976-1978 Estimates versus 1994 Low Resolution Core Estimates

The 1976-1978 and 1994 data taken below the TI Dam represent focused sampling programs centered on the areas of greatest PCB contamination. In particular, the low resolution coring program was centered on a limited number of *hot spots*, so as to provide a basis for comparison to the earlier survey without duplicating the scale of the effort.

In order to make a comparison between the two surveys, a common sampling basis had to be established. Clearly defined *hot spot* areas were needed to divide samples into those outside and inside the *hot spot* areas. The original report (Tofflemire and Quinn, 1979) did not provide maps with sufficient resolution so as to permit a clear definition of the *hot spot* boundaries. The 1992 MPI report defined a series of smaller areas, called dredge locations, whose borders approximated those of the original *hot spots*. Twelve dredge locations were used to represent the seven *hot spots* surveyed during the low resolution coring program. Using these borders, both NYSDEC and Phase 2 sampling locations were designated as internal or external to the area.

This procedure was used to designate sample association for *Hot Spots* 25, 28, 31, 34, 35, 37, and 39, the seven *hot spots* studied by the low resolution coring program. Incidentally, one of the areas covered by the exploratory cores (TAMS location 42) also coincided with MPI dredge location 182. This area was added to the evaluation of sediment inventories, bringing the total number of dredge locations to 13. Within these areas, MPI identified 111 points. However, upon review of the maps supplied in MPI (1992), two additional points were noted in *Hot Spot* 37, yielding a total of 113 sampling locations from 1976-1978. The low resolution coring study occupied 64 coring locations from within these areas. Plates 4-21 to 4-28 show the 1992 MPI dredge location areas as well as the sampling locations for both sampling programs.

To compare the PCB levels within these areas, arithmetic and geometric means were calculated. Because of the log-normal nature of the data distribution for both data sets, the geometric mean and its standard error provide the best statistical basis to assess change in the sediment inventories over time. The log-normal nature of the entire 1976-1978 data set was originally established by Tofflemire and Quinn (1979). The subset of 113 NYSDEC samples was also log-normally distributed, as seen in Figures 4.2-3 and 4.2-4. These figures show that both the one-foot length-weighted averages (LWA) and the SSW-corrected PCB mass per unit area estimates (MPA) are log-normally distributed. Similarly, Figures 4.2-3 and 4.2-4 show the LWA and MPA distributions for the subset of 64 low resolution cores from the seven study areas below the TI Dam as well as for all low resolution core results below the TI Dam. These results were determined to be log-normally distributed using the Shapiro-Wilk W test for normality (Table 4-6).

Geometric means were compared in log space to determine the statistical significance of changes in the sediment inventories. That is, the average of the log-transformed values for each *hot spot* or dredge area for the 1976-1978 survey was compared to the average of the log-transformed values for the same *hot spot* or dredge area based on the 1994 low resolution coring study. The geometric mean (\overline{C}_G) was calculated as follows:

$$\overline{C}_G = e^{\left(\frac{1}{n} \sum_{i=1}^n \ln(C_i) \right)} \quad (4.2-1)$$

where: C_i = LWA or MPA for each sampling location in a *hot spot* or dredge area;
 n = number of samples in the *hot spot* or dredge area;
 $\frac{1}{n} \sum_{i=1}^n \ln(C_i)$ = mean log for the *hot spot* or dredge location; and
 $\ln(C_i)$ = natural log of C_i .

The comparisons were made using the Tukey-Kramer honestly significant difference test (JMP, 1994) which tests for the statistical significance of the difference between means of sample populations when the populations are normally distributed. In this instance, data were normalized by performing a log-transformation. Non-parametric tests (*i.e.*, tests that do not require a normal distribution) were also used to test for differences between populations.

Although the geometric mean and log-transformed data provide the best basis for establishing the occurrence of change in the sediment PCB inventory, the arithmetic mean must be used if the degree of change is needed. The arithmetic mean for the LWA values can be determined in two ways as follows:

$$1. \quad \text{Arithmetic Mean } (\bar{C}_A) = \frac{1}{n} \sum_{i=1}^n C_i \quad (4.2-2)$$

where: C_i = LWA or MPA
 n = number of samples in study areas;

$$2. \quad \text{Arithmetic Mean } \left(\bar{C}_A' \right) = e^{\frac{1}{n} \sum_{i=1}^n \ln(C_i)} * \Psi_n \left(\frac{S_y^2}{2} \right) \quad (4.2-3)$$

where: C_i , n , and $\ln(C_i)$ are defined as above,
 S_y^2 = variance of the sample log values, and
 $\Psi_n(t)$ = an infinite series as follows:

$$\Psi_n(t) = 1 + \frac{(n-1)t}{n} + \frac{(n-1)^3 t^2}{2! n^2 (n+1)} + \frac{(n-1)^5 t^3}{3! n^3 (n+1)(n+3)} + \frac{(n-1)^7 t^4}{4! n^4 (n+1)(n+3)(n+5)} + \dots \quad (4.2-4)$$

$$\text{where: } t = \frac{S_y^2}{2}$$

The first formula represents the simple arithmetic mean of the data. Given the log-normal distribution of the data set and the limited number of samples for each *hot spot* or dredge location, this formula does not provide an unbiased estimate of the true arithmetic mean. However, it is possible to take advantage of the knowledge that the underlying data set is log-normal. The second formula represents a minimum variance, unbiased estimation of the arithmetic mean, given that the underlying distribution is log-normally distributed (Gilbert, 1987). It is also possible to obtain the standard error of the estimator, given the same assumptions about the data set. The standard error of the arithmetic mean is calculated as $\frac{1}{\sqrt{n}}$.

$$\bar{S}'_A = \left[\left[\Psi_n \left(\frac{S_y^2}{2} \right) \right]^2 - \Psi_n \left[\frac{S_y^2 (n-2)}{n-1} \right] * \frac{2}{n} \sum_{i=1}^n \ln(C_i) \right]^{\frac{1}{2}} \quad (4.2-5)$$

where: C_i , n , 1_n , t and S_y^2 defined as above. Table 4-7 provides a summation of the geometric and arithmetic means.

The relationship among the three estimates can be expressed as $\bar{C}_G < \bar{C}_A \leq \bar{C}'_A$. The geometric mean is less than the simple arithmetic mean which is less than or equal to the minimum variance unbiased estimate of the arithmetic mean. This relationship holds in all *hot spots* for both the length-weighted average (LWA) and the PCB mass per unit area (MPA) except for *Hot Spots* 25 and 39 for the 1976-1978 data and *Hot Spots* 34 and 35 for the 1994 data. In each of these cases, the unbiased estimate (\bar{C}'_A) was roughly 5 to 10 percent lower than the simple arithmetic mean (\bar{C}_A). The geometric mean (\bar{C}_G) was substantially smaller than the arithmetic mean, which is typically characteristic of log-normal distributions.

Using the log-transformed data, the 13 dredge locations were evaluated for statistically significant changes in the PCB levels between the 1976-1978 and 1994 surveys. This evaluation is summarized in Figure 4-21. The figure presents the geometric mean values with error bars representing two standard errors about the mean. Each paired set was tested for statistically significant difference using the Tukey-Kramer honestly significant difference (JMP, 1994). Statistically different values are represented by larger, solid markers. In this evaluation, only three of the thirteen dredge locations were found to be different based on LWA, and only four differed based on MPA. This lack of statistical significance was due in part to the very limited data set available for each dredge location. However, when grouped on a *hot spot* basis, a larger fraction of the areas was shown to be statistically different. These results are summarized in Figure 4-22. (Appendix F provides summary statistical data which form the basis for the information displayed in Figure 4-22).

Five of the eight study areas were statistically different for LWA, the length-weighted average PCB concentration for shallow sediments. Of these, four showed decreases in concentration from 1976-1978 to 1994 conditions while one indicated increased PCB concentrations. The remaining three areas were unchanged. Similarly, four of the eight study areas, with three declining and one

increasing, were statistically different for MPA. These four areas corresponded to four of the five areas with significant changes in LWA.

The implications of the changes in MPA are straightforward. Decreases in MPA correspond directly to decreases in the inventory of PCBs within the sediment and vice versa. The interpretation of the changes in MPA is summarized in Table 4-8 for each of the *hot spot* areas. The tables provide the surface area, number of samples, MPA, and PCB inventory in kilograms for each of the *hot spots* under 1976-1978 and 1994 conditions. The MPA given in Table 4-8 is the unbiased minimum variance estimator of the arithmetic mean and not the geometric mean represented in Figure 4-22. As noted previously, the arithmetic mean is needed to estimate the inventory while the geometric mean is used to discern statistically significant changes. It should also be noted that the 1976-1978 conditions are calculated using the solid specific weight correction described earlier. The original MPI (1992) inventory estimates are provided in Table 4-8, in addition to the 1976-1978 sediment inventories recalculated for this report.

The PCB inventories were calculated for both the 1976-1978 and 1994 results using the same area and the minimum variance unbiased estimator for the arithmetic mean on an individual *hot spot* basis. In this manner, the magnitude of the change in PCB inventory in each *hot spot* between the two sampling events could be estimated.

Table 4-8 provides important information on the scale of the *hot spot* inventory changes. All of the statistically significant changes represent differences of a factor of two or higher, *i.e.*, statistically significant increases represent at least a doubling of the 1976-1978 sediment PCB inventory, while decreases represent at least a halving of the 1976-1978 sediment PCB inventory. In fact, most of these changes are even greater. Specifically, the inventories at *Hot Spots* 31, 34, and 37 have declined by approximately five-fold, two-fold, and three-fold, respectively, while the inventory at *Hot Spot* 28 has increased eleven-fold. The remaining four *hot spot* inventories appear unchanged with relatively good agreement (less than 10 percent difference) between 1976-1978 and 1994 for three of the four areas. The fourth area, *Hot Spot* 39, had a large, but not significant, increase in PCB inventory. Overall, the surveyed areas increased in PCB inventory over the study period, as shown at the bottom of Table 4-8. However, the nature of this gain warrants further discussion.

The procedures to estimate the MPA and sediment inventory differed between the 1976-1978 and 1994 sampling programs. The earlier program relied on extrapolation to calculate the total PCB inventory, while the 1994 program did not. The 1976-1978 program used a limited number of long cores that completely encompassed the entire PCB inventory as a basis to vertically extrapolate the large number of grab samples obtained. These grab samples were assumed to represent sediments from 0 to 4-inches in depth. Extrapolation factors for the grab samples were developed separately for each reach by both Tofflemire and Quinn (1979) and MPI (1992). Table 4-9 shows the distribution of grab and core samples for the 1976-1978 data set. There is an inherent uncertainty associated with the estimation process, since the correct extrapolation for each individual grab sample is not known. However, the individual cores do provide a basis for a realistic assessment of this uncertainty.

Figure 4-23, derived from MPI (1992) and the Hudson River Database Release 3.5, represents the relationships among the 0 to 4-inch section, the 0 to 12-inch section, and the entire core for the 1976-1978 data. The data is grouped by location above or below Lock 5. The intercept in each regression was not statistically different from zero, so the lines were forced through zero. From these diagrams, it is apparent that the extrapolation of the 0-4-inch section to the 0-12-inch section should on average be within 6 to 8 percent of the true value when groups of samples are considered. The diagram also indicates that no systematic bias exists. The error on individual cores is larger (42 mg/kg above Lock 5 and 16 mg/kg below Lock 5) based on the intercepts of the individual 95% confidence limits.

The MPA for the 0-12-inch section of the entire core yields slopes >1 in both instances indicating that a portion of the mass is unaccounted for in the 1976-1978 estimates. The error in the individual points and the regression line is small for the cores below Lock 5, 2 g/m^2 on individual cores and 10 percent on the regression line. For points above Lock 5, the error on both the regression line (30 percent) and on individual cores (61 g/m^2) is much greater.

For the 1994 low resolution core collection and interpretation, extrapolation was not necessary, since most cores collected were complete. ^{137}Cs was used to assess core completeness as discussed previously in Chapter 2. Although some cores were defined as incomplete, these cores are typically scattered throughout the data set and do not greatly impact the vertical integration of PCB mass, *i.e.*, nearby complete cores of comparable thickness suggest that little PCB inventory was

missed by the incomplete cores. Table 4-9 presents the number of complete and incomplete cores for each *hot spot* for the 1994 data set. Additional factors indicating near-completeness in a core include the PCB profile itself (Chapter 2) and the trend of ^{137}Cs between surface (0 to 1-inch) and bottom core segments.

Given the relatively well-known ^{137}Cs impact to the Hudson watershed as recorded in the various high resolution cores, as well as by various authors (*e.g.*, Bopp and Simpson, 1989), the trend in ^{137}Cs levels between surface and deep sediments can yield useful information about the core. As can be seen in Figure 4-24, both ^{137}Cs and PCB have seen substantive maximum concentrations relative to the oldest and most recent deposition. In ^{137}Cs in particular, the surface sediments are substantially higher in concentration than the sediments deposited in the mid-1950s. Assuming that this kind of ^{137}Cs distribution applies in a rough manner to all Hudson River locations, if surface ^{137}Cs levels are higher than those at the bottom of the core, then it is highly likely that the core encompasses the entire section of recent deposition. This is because ^{137}Cs levels have not yet dropped to the levels seen in the mid-1950s. Thus, the core bottom is close to the early 1950s horizon and little post-1950 deposition lies below it.

Conversely, when ^{137}Cs increases from top to bottom in a low resolution core, it is unclear how much recent sediment lies below the core since higher ^{137}Cs levels relative to the surface layer exist from 1992 depositions back to the early 1960s. Ideally in an incomplete core, falling ^{137}Cs levels from surface to bottom indicate that little recent deposition lies below the core and that the core is nearly complete. Rising ^{137}Cs levels with depth indicate that much recent deposition may lie below the core bottom. Table 4-9 provides a summary of the ^{137}Cs trends for the incomplete cores. *Hot Spots* 25, 28, and 31 have a large majority of complete cores and so these inventory estimates should be accurate. *Hot Spots* 34, 35, 37, and dredge location 182 have a relatively large proportion of incomplete cores, but most are characterized by falling ^{137}Cs , indicating near-completeness in the cores and subsequently relatively accurate inventories. Only *Hot Spot* 39 has a large proportion of incomplete cores with rising ^{137}Cs . Estimation of an accurate inventory is difficult here but it is still possible to assess the change at *Hot Spot* 39, as discussed later in this section.

Returning to the discussion of *hot spot* inventory changes, it is evident that several of the smaller *hot spots* have lost a substantial portion of the 1976-1978 PCB inventory. These *hot spots* are

shown in Plates 4-23, 4-24, and 4-25. More than five metric tons (5,040 kg) were represented in *Hot Spots* 31, 34, and 37 in 1976 to 1978, based on the MPA calculations presented in this report (Table 4-8). This substantial mass is still less than the MPI (1992) estimate of almost seven metric tons (6,830 kg) based on a constant SSW of 1 g/cc (Table 4-8). In 1994, the best estimate of 5,040 kg in these areas was reduced to only 1,881 kg, a loss of 63 percent. This loss is well beyond any dechlorination process (maximum mass loss of 26 percent) and must therefore, represent the re-release of PCBs from the sediment to the water column via one or more processes. The exact mechanism or mechanisms responsible for this release are not well known but the effect in these areas is quite profound.

Given the relatively thin depth of recent (post-1954) deposition in these *hot spots* (less than 12-inches; see Table 4-10 and Appendix D), resuspension of river sediment is certainly a viable mechanism. Ground water advection or biologically driven losses are also possible. A portion of this apparent loss may be due to differences in quantitation techniques, but it is highly unlikely that quantitation differences could account for such a substantial loss.

Of particular note among these three areas is *Hot Spot* 37. Although the samples contained strictly within the dredge boundaries yielded a statistically significant loss, a core collected just downstream yielded a very high MPA of 125 g/m² as compared to 17 g/m² for the *hot spot* itself in 1994. This core appears to be within the original *hot spot* boundary defined in Tofflemire and Quinn (1979). These results suggest that this area may be a source of the large PCB load increase described in the DEIR (TAMS et al., 1997) for water column Transect 3. A high flow event in the Hoosic River, the mouth of which is immediately upstream of *Hot Spot* 37, may have remobilized material from the upstream end of *Hot Spot* 37. The frequency of similar high flow events in Hoosic River suggests that this *Hot Spot* may continue to be a source of PCBs downstream in the water column.

Hot Spot 28 near the downstream entrance to Lock 6 (see Plate 4-22) exhibited a statistically significant gain in PCB inventory. PCB inventory increased from just under two metric tons (1,850 kg) to over 20 metric tons (20,390 kg). The 1994 core profiles for *Hot Spot* 28 typically exhibited two forms, as shown in Figure 4-25. In Profile 1, the coring site has apparently seen substantial deposition over time, burying the more contaminated PCB layers. In this profile, peak concentrations reach 526 mg/kg, but are under and overlain by sediments at lower concentrations. The PCB concentration in the

thickly sliced core in Profile 1 matches the better resolved high resolution cores collected in 1992 (Figure 4-24), but the shallow sediments (0 to 12-inches) still represent a substantial PCB concentration (145 mg/kg). Therefore, although burial of the highest sediment concentrations is occurring, the more recently deposited material bears a substantial PCB contamination level of its own and is not considered “clean”. Core profiles LH-28F, LH-28I, and LH-28K in Appendix D have conditions similar to Profile 1.

In Profile 2, the overlying lower PCB level sediments are missing and apparently peak PCB concentrations are at or very near the surface. This type of profile can occur when sediment deposition effectively stops at a given location, leaving highly contaminated sediments at the surface. This profile can also be found in areas undergoing scour, where the upper layer in Profile 1 has been removed and the river is now scouring peak PCB concentration at the coring location. In either case, sediment burial is not occurring. Consequently the potential for PCB re-release at these sites is very high and may be on-going. Cores LH-28E, LH-28G, LH-28J, and LH-28N in Appendix D have similar profiles. It was noted that the ⁷Be levels were detected in surficial sediments at all of these locations, indicating recent deposition. This evidence for recent deposition apparently contradicts the strong PCB profile evidence for long-term sediment loss or lack of burial. One likely explanation is that the area is subject to sporadic scour events followed by periods of deposition. This would provide a thin layer of ⁷Be-bearing material at the surface which would be removed periodically along with some of the underlying material during scour events.

Although the PCB inventory has apparently increased at *Hot Spot* 28, its long term storage there is clearly not assured. In addition, the burial process to date has clearly not yielded clean overlying sediments. More than likely, the PCB contamination seen in the shallow sediments of Profile 1 is the result of PCB re-release from sediments further upstream and from PCB released from the GE Hudson Falls facility as well as from local re-release from the *hot spot* itself. *Hot Spot* 28 does not suggest a steady rate of deposition so as to sequester contaminated sediment, instead the burial, subsequent re-working, and re-release of the contaminated sediment by the river appears to be continuous and on-going.

It is most likely that the apparent increase in total inventory is the result of an underestimate of PCB inventory in 1976-1978 derived from cores of insufficient length and incorrect assumptions about the total depth of PCB contamination. The percent mass deposited between 1977 and 1994 can be

estimated using the dated high resolution cores shown in Figure 4-24. These cores are considered recorders of river PCB loads, as described in the DEIR (TAMS, *et al*, 1997). In these and essentially all other dated sediment cores from the Hudson, the sediment record shows a substantial decline over time in the PCB loads carried by the river. Based on these core profiles, only 2 to 5 percent of the cumulative PCB load was transported in the period after 1977. Thus the river was not carrying the volume of PCBs which would be required to substantially raise sediment inventories between 1977 and 1994. Since at the time of the 1976-1978 surveys the river had already transported at least 95 percent of its total PCB load, it is highly unlikely that the remaining 2 to 5 percent to be transported in the post-1978 period could yield the eleven-fold increase in inventory found in *Hot Spot 28*. Thus, it is unlikely that a true substantive increase in PCB inventory has occurred at *Hot Spot 28* since 1976-1978. Rather, it is likely that the 1976-1978 inventory was badly underestimated.

At the same time, the on-going reworking and re-release process indicated by the core profiles is born out by the changes in the shallow-sediment concentrations (LWA). Both the total sediment inventory and the shallow sediment inventory as represented by LWA have substantially increased (see Table 4-10). Given that the PCB input history to the sediment is similar to that recorded in the high resolution cores as shown in Figure 4-24, an increasing shallow sediment inventory is inconsistent with an increasing total sediment inventory. Specifically, the 1976-1978 cores were collected just after the PCB maximum seen in the high resolution cores. Thus, after the 1976-1978 period, PCB concentrations in sediment have been declining. In locations where true burial occurs between 1976 to 1978, the total sediment inventory should increase as additional contaminated sediment is deposited above the mid-1970s peak concentration. However, the shallow sediment concentration (LWA) should decline as the less contaminated sediments overlay the sediments previously deposited. This is not the case in *Hot Spot 28* where shallow sediment concentrations have increased six-fold.

While it is also true that upstream inventories of PCBs have also declined and could thus provide some additional material to *Hot Spot 28*, it is unlikely that this process is responsible for the eleven-fold increase noted. Specifically, upstream resuspended sediment would be mixed with the sediment load already carried by the river, thus downstream transport serves to dilute the sediment concentrations. Yet shallow sediment concentrations are comparable or higher than many of the core locations occupied upstream. Also, it is likely that any major transport event sufficient to substantially

increase the sediment inventory at *Hot Spot 28* to this degree would be recorded in the nearby high resolution cores. High resolution core 18 was collected near the downstream end of *Hot Spot 28* at Rm 185.8. This core clearly shows that the majority of PCB transport occurred prior to 1978 and that deposited sediment concentrations are declining over time. This contradicts the observation that shallow sediment concentrations have increased at this *hot spot* since 1978.

Both the Phase 2 water column and high resolution core analysis demonstrated the absence of local sources in the vicinity of *Hot Spot 28*. In the absence of local PCB input, increases in both shallow sediment and total sediment inventories can only occur when both PCB deposition and PCB re-release (probably via scour) are occurring or have occurred during the intervening period. Based on the number of cores similar to Profile 1 in Figure 4-25, it appears that slightly less than half (4 of 10) of the coring sites in *Hot Spot 28* are undergoing burial with less contaminated, but hardly clean sediments. However, a similar fraction of sites (5 of 10) is undergoing scour, thus bringing the peak PCB concentrations back to the surface.

Conditions at *Hot Spot 28* can be contrasted with those at *Hot Spot 39*. At this *hot spot* the shallow sediment inventory has shown statistically significant decline of about 30 percent (1.4-fold decrease). This is matched by a three-fold increase in mass which is not statistically significant. *Hot Spot 39* contained only six complete cores out of a total of 14. Of the six complete cores, five yield profiles similar to Profile 1 in Figure 4-25, indicating steady deposition and burial. Four incomplete cores yield profiles with rising ^{137}Cs and rising PCB, indicating that a potentially significant portion of recent sediment and PCB inventory is present below the coring depth. Only two cores yield profiles similar to Profile 2 in Figure 4-25 and the remaining cores indicate little activity, with the PCB inventory contained almost entirely in the shallow sediments. Thus nine of 14 cores indicate that burial of PCB bearing sediments is the predominant process at *Hot Spot 39*. Shallow sediment concentrations indicate that the depositing sediments are not clean, with PCB concentrations in the range of 4 to 62 mg/kg with a median of about 5 mg/kg. *Hot Spot 39* represents the only *hot spot* study area to exhibit a consistent PCB burial process. Unfortunately, an accurate estimate of the inventory gain could not be made, due in part to the large number of incomplete cores. Also, the 1976-1977 estimates are based on short cores and grabs which would underestimate the PCB mass. Based on the results available, the apparent gain is at least a three-fold increase.

The remaining three study areas, *Hot Spots* 25 and 35, and dredge location 182 were characterized as unchanged. Plates 4-21, 4-24, and 4-27 show the sampling locations associated with each area. Two of these areas are particularly limited in sample coverage. Specifically *Hot Spot* 35 and dredge location 182 have only four and two samples collected, respectively, in 1994 as compared to 11 and six samples, respectively, collected in 1976 to 1978. Thus, statistical analyses of these two areas are quite limited, especially for the dredge location 182. However, taken together, these areas still provide useful information on relatively unchanged areas.

As shown in Table 4-8, the PCB inventory estimates for 1976-1978 and 1994 are quite close in the areas characterized as unchanged, within 10 percent of each other in each case. The apparent lack of change is borne out by the core profiles shown in Appendix D. Figure 4-26 shows two core profiles typical of these areas. In general, these areas are characterized by profiles where little PCB mass occurs below the top core segment. These profiles appear somewhat similar to Profile 2 in Figure 4-25, but there is an important distinction. Cores from *Hot Spots* 25, 35, and dredge location 182 show a much greater level of change between the shallow sediment segment and the underlying layer. Typically, the PCB inventory in the underlying layer is at least five times less than the shallow sediment layer and is frequently zero. This would suggest that only a shallow PCB inventory exists at these *hot spots*. No cores from within these areas exhibited the PCB burial profile typically seen in *Hot Spot* 39. Although several cores in these areas were not complete (see Table 4-9), all incomplete cores were characterized with falling ^{137}Cs levels, thus the majority of recent sediment was captured in the core. The finding that in many *hot spots* the current PCB inventory is in shallow sediments indicates that:

- Burial of these *hot spots* is not occurring;
- Opportunity for remobilization of PCBs is present; and
- There are little or few overlying clean sediments to remove to get to contaminated sediments.

4.2.4 ⁷Be in Surface Sediments

It was originally hoped that the presence or absence of ⁷Be in the 0 to 1-inch layer of a low resolution core would provide some information on the occurrence of sediment scour, since ⁷Be is generally detected in more recently deposited sediments. While the absence of ⁷Be does not preclude the presence of sediment less than six months old, little direct correlation could be found between ⁷Be presence/absence and sediment deposition or scour. This is evident in the four core profiles presented in Figures 4-25 and 4-26 that all have ⁷Be present, yet are distinctly different. These profiles characterize deposition (burial), scour, and no net change. On an individual basis, ⁷Be does not appear to be able to separate these environments, but this does not imply that the ⁷Be data are of no use. When viewed on a *hot spot* area basis, it is apparent that *Hot Spot 37*, which has undergone PCB inventory loss, has a distinctly lower detection frequency for ⁷Be (3 of 11 core sites or 36 percent) as compared to the depositional environment around *Hot Spot 39* (13 of 14 sites or 93 percent). (See Plates 4-25 and 4-26).

On average, the three *hot spots* exhibiting PCB loss had a lower average frequency of ⁷Be detection (0.54) than the two *hot spots* with mass increases (0.87). Although these data sets are too small to perform statistical analysis, the average values support this general correlation. The three *hot spots* with unchanged inventories yielded a wide range of ⁷Be detection frequencies. However, the number of points available for these areas is quite limited and so they were not examined further for ⁷Be. All the ⁷Be data in terms of presence/absence for the *hot spots* sampled as shown in Plates 4-21 through 4-28.

Because of the nature of its geochemistry and short half life, ⁷Be still provides the potential to prove the presence of less than six-month old sediments. However, presence of six-month old sediment at time of collection does not guarantee a complete depositional record in the core. In many instances ⁷Be was present in cores from *hot spots* with declining PCB inventories such as *Hot Spots 31* and *35*, indicating that it is not a perfect predictor for PCB loss environments. Taken on an area basis however, ⁷Be frequency of detection was lowest for areas of PCB inventory loss and highest for areas of inventory gain, as might be expected.

4.2.5 *Hot Spot* Boundaries

A subset of cores was collected just beyond the original *hot spot* boundary so as to assess the accuracy of the boundary as drawn. While in most instances PCB inventories were lower in the cores external to the hot spot or dredge location, there were some important exceptions including the four TAMS exploration areas (cores labeled LH-41, 42, 43, and 44). Twenty-eight cores were sited outside *hot spot* or dredge locations. Of these, 21 yielded relatively low PCB concentrations. The range of the LWA values (representing sediments from 0 to 12-inches) for the 21 cores was 1 to 27 mg/kg with a median value of 12 mg/kg. Two of these cores had larger inventories at depth and were associated with *Hot Spot* 39 and dredge location 182. The remaining seven cores with elevated concentrations were associated with *Hot Spots* 28, 31, 34, 37, dredge location 182, and TAMS location 41. The range of LWA for these cores was 46 to 709 mg/kg with a median value of 126 mg/kg. For *Hot Spots* 28, 31, and 34, the elevated sediment concentrations were found outside the *hot spot* boundary but still within the same sediment type as classified by the side-scan sonar interpretation. These cores would suggest that the dredge location boundaries may need to be expanded to encompass more of the same sediment type in the vicinity of the dredge location.

4.2.6 Comparison of the 1994 *Hot Spot* Inventories with Other 1977 Estimates

The estimates of total PCB quantities in the *hot spots* must be presented on a consistent basis for the comparisons to be meaningful. Table 4-11 presents the estimates of Malcolm Pirnie (1979), Tofflemire and Quinn (1979), Malcolm Pirnie (1992), and an estimate derived by TAMS from the data provided in Malcolm Pirnie, 1992. The appropriate low resolution core total PCBs quantities are derived by multiplying the *hot spot* area used in the 1976-1978 estimate by the 1994 mean MPA. The 1976-1978 estimates of the inventory are presented and corrected using a solid specific weight (SSW) based on the mean total PCB concentration for the *hot spot*. These SSW values are obtained from Table 4-3 rather than accept the original author's assumption of an SSW of 1 g/cc. Results are compared via a Delta function, where:

$$\Delta_i = \left(\frac{1994 \text{ Low Resolution PCB Quantity} - (1976-1978) \text{ Revised PCB Quantity}}{(1976-1978) \text{ Revised PCB Quantity}} \right) * 100\% \quad (4.2-6)$$

In this manner, Δ_i (%) is negative for losses and positive for gain. A Δ_i of 100% represents a doubling of the 1976-1978 PCB inventory. A Δ_i of -50% represents a halving of that inventory.

Differences between the 1976-1978 and 1994 estimates of more than a factor two are considered significant and likely to be beyond the level of uncertainty. *Hot Spots* 25 and 35 lack significant differences for all inventory estimate comparisons. *Hot Spots* 28, 31, 34, and 37 have significant differences for each estimate with only 28 showing a gain and the others loss. The losses are considered definitive because the 1976-1978 estimates may be biased low due to insufficient depth of cores as discussed previously in Section 4.2.3. Thus the estimated 1994-1977 mass loss represents a minimum estimate of the actual mass loss. Overall, six of the seven *hot spots* inventories have a consistent level and direction of change for all four comparisons. That is *Hot Spots* 31, 34, and 37 show losses greater than 50 percent of the 1976-1978 inventory, *Hot Spots* 25 and 35 appear to be unchanged or to have lost no more than a 40 percent and *Hot Spot* 28 has had a large apparent increase.

Only *Hot Spot* 39 shows an insignificant loss in the Malcolm Pirnie (1978) estimate and a significant gain in both estimates using the Malcolm Pirnie (1992) data. This *hot spot* shows considerable levels of PCB contamination at more than two feet of depth including eight incomplete cores. Of these eight, five have rising ^{137}Cs levels strongly indicating that more contamination lies below. The Malcolm Pirnie (1992) estimate considered only the shallow sediments and therefore, underestimated the inventory. The MPI (1978) estimate includes the values at depth and yields no significant change in inventory for *Hot Spot* 39 to 1994. However, the MPI (1978) estimate is based on only about one-quarter of the surface area for the *hot spot*, i.e., 26, 400 m² for the MPI (1978) estimate and 105,700 m² for the MPI (1992) estimate. Thus, the absolute inventories given by MPI (1978) and other 1976-1978 estimates are not very different. Although the MPI (1978) estimate was based on deeper samples, it is still an underestimate of the current inventory as given in the last section of Table 4-11.

The inventory of *Hot Spot* 28 appears to have increased between 1.5 and 10 times between 1976-1978 and 1994. The 1994 estimates range from 18-20 metric tons of total PCBs in *Hot Spot* 28 which is comparable in scale to the 23.2 metric ton estimate for the entire TI Pool inventory given by

M. Brown *et al.* (1988) . Like Hot Spot 39, the inventory may have been present but missed by incomplete cores in the 1976-1978 sediment survey. The 1976-1978 estimates are probably biased low due to insufficient core depth causing the true gain to be less than measured due to failure to core the entire profile.

As discussed in Section 4.2.3, the issue of sediment inventory gain is particularly sensitive to the accuracy of the original core collection. If earlier cores were not collected from a sufficient depth, then the 1994 results will show an apparent inventory gain which is not real. An examination of the high resolution cores presented in Figure 4-23 shows that most PCB deposition occurred prior to 1977. In fact, based on the two cores shown which were collected from this area of the Hudson, roughly 95 percent or more of the sediment inventory was deposited prior to 1977. Thus the reported inventory gains of 194 to 1040 percent for *Hot Spots* 28 and 39 seem highly unlikely, particularly given the observed PCB peak concentration which is in the hundreds of mg/kg. The high resolution cores indicate that sediments of this level of contamination were last deposited in the 1970s. Nothing since 1980 has exceeded the 100 mg/kg level.

In summary, this analysis of *hot spot* inventories shows a consistent pattern of loss of at least 50 percent of the 1977 inventories for *Hot Spot* areas 31, 34, and 37 regardless of the source of the original estimate. *Hot Spots* 25 and 35 appear to be basically intact or at least have lost no more than 40 percent, again regardless of the source of the original estimate. Inventories for *Hot Spots* 28 and 39 in 1994 are distinctly higher than the 1977 estimates. A small portion of this gain may be due to post-1977 deposition. However, it appears that the majority of this gain is likely due to inaccurate estimates derived from cores of insufficient length to capture the post-1954 recent sediment profile. The best estimate for the 1994 sediment inventories is given in Table 4-12. A total of 27.3 metric tons of PCBs resides in these *hot spots* with *Hot Spot* 28 representing the vast, previously undocumented, majority of this material.

4.3 Sediment Contamination in the Near-Shore Environment

As part of the low resolution coring program in the Thompson Island Pool, several clusters of samples were located in near-shore areas, approximately within 50 ft of shore. Part of this program was to assess the level of PCB contamination in areas where direct sediment exposure to local populations was likely. As a part of this program, cores were collected from 4

cluster locations with 1 or five cores per location. The specific clusters were numbers 16, 17, 18 and 19. These locations can be seen on Plate 2-1. On the plate, the clusters are denoted as “LR-xx” where xx is the cluster number. Three of the clusters (16, 18, and 19) are located around Griffin Island and one (17) is located about 1 mile upstream across from *hot spot* 8. Two of these cluster locations (16 and 18) had a single previous NYSDEC coring location which became the center of the cluster when locating the coring locations.

The reference point for comparison with these data was the estimated PCB concentration derived for the Phase 1 Report (TAMS/Gradient, 1991) which used a value of 66 mg/kg as the exposure point concentration for human exposure in the preliminary risk assessment. This value represented the 95 percent confidence interval of the arithmetic mean of the shallow sediment concentrations based on the 1984 NYSDEC sediment collection effort. Concern with this estimate stemmed from its basis on the entire sediment 1984 data set, potentially underestimating near-shore exposure concentrations.

To address this issue to a limited degree, the low resolution sediment coring program obtained cores from 4 near-shore areas in the TI Pool . Due to some limitations in the accessibility of the shoreline area, not all near-shore cluster cores were located within 50 ft of shore. On this basis, a subset of the original 16 near-shore cores was analyzed based on their proximity to the shoreline. A distance of 50 ft was chosen since it approximated a water depth of 4 ft, a likely water depth for wading and swimming. This yielded 11 low resolution cores from these clusters. The results from this subset are shown in Table 4-13. The 95 percent confidence limit value (151) is substantially greater than the original estimate used in the Phase 1 report. Its usefulness may be limited, however, due to the small sample size. Also represented in the table are the minimum, maximum, geometric mean, arithmetic mean and an unbiased, minimum variance estimator (MVUE) of the arithmetic mean. The MVUE represents the best estimate of the arithmetic mean, given that the underlying data distribution is log-normal. This property of the PCB data was discussed previously in this report and is not repeated here. The 95 percent confidence interval is the value typically used in risk assessment calculations.

A second approach to estimating the near-shore sediment concentrations for the TI Pool was made by considering all near-shore, fine-grained, low resolution TI Pool cores within 50 ft of shore. This yielded a larger data set (19 cores) as well as a higher 95 percent confidence limit (264 mg/kg). The assignment of sediment classification was based on the classifications obtained from the side-scan sonar results described previously in this report and the DEIR. The results from the two low resolution data groupings were not statistically different as might be expected since many sample locations were common to both groups.

As a last approach, the 1984 NYSDEC data set was examined on the same basis, *i.e.*, fine-grained sediment cores as classified by side-scan sonar within 50 ft of shore. These results yielded values similar to those obtained from the low resolution cores.

In each approach, it is apparent that the original estimate of 66 mg/kg for near-shore sediment exposure in the preliminary risk assessment was too low and that a value in the range of 135 to 264 would be more appropriate. Given that the original risk estimate did not exceed the USEPA acceptable range, it is unlikely that the revised range will represent an unacceptable risk. These results will be reviewed and incorporated in the Phase 2 risk assessment as part of the human health risk assessment.

4.4 Summary and Conclusions

4.4.1 Sediment and PCB Inventories in the TI Pool

Sediment core profiles obtained in 1994 exhibited a range of characteristics from inventory gain to loss relative to the original 1984 core profiles, with sediment inventory loss being the most common. Some 1984-1994 core pairs strongly suggested sediment scour, based on the apparent upward vertical movement of the PCB contamination horizon.

The 1984 sediment survey results are best characterized as the sum of trichloro and higher chlorinated homologues when a correction factor of 0.934 is applied. The 1994 data showed a linear decline in the STri+ inventory when plotted against the original 1984 inventory. This loss was attributed to both dechlorination and to re-release to the water column

Using two different estimates for molecular weight, an estimate for the 1984 sediment STri+ molar inventory was obtained. This estimate was used to track PCB loss to the water column from the sediment relative to dechlorination loss over the period 1984 to 1994.

When sediment inventories were grouped by the 1984 STri+ inventory as greater than or less than 10 g/m², a statistically significant trend in the relative inventory change was found. Specifically, sediments greater than 10g/m² yielded inventory losses of about 39 percent. Of this 28 percent was attributed to PCB re-release to the water column and 12 percent was attributed to dechlorination. The estimates of 28 and 39 percent represented lower bounds on the actual PCB losses.

The scale of the PCB loss from these sediments is of similar magnitude to the water column inventory gains reported in the DEIR. These results confirm and support the contention put forth in the DEIR that TI Pool sediments contribute directly and substantively to the water column load. For sediments less than 10g/m², an upper bound on the sediment gain was obtained, at between 87 and 104 percent. Presumably these gains, if real, are due to deposition of PCBs from sediment re-release as well as upstream inputs.

Based on these trends, the river is apparently re-distributing the sediment PCB inventory. Little evidence for extensive sediment burial was found in the TI Pool. More core sites exhibited loss than gain or burial. Instead, it appears that the PCB inventories of the more contaminated sediments are being redistributed, ensuring that the burial of contaminated sediments with clean sediments is not occurring. These same processes would also serve to deliver PCBs to the water column and produce the loads recorded by both USEPA and GE monitoring.

4.4.2 Sediments and PCB Inventories Below the TI Dam

- Comparison of the texture type indicated by the sonar images with the 1976-1978 NYSDEC sediment survey grain-size data found good agreement. This suggests that the river bottom depositional types remain constant.
- Malcolm Pirnie, Inc. (MPI, 1978), Tofflemire and Quinn (1979), and MPI (1992) provided estimates of the 1976-1978 total PCB inventory in *hot spots* located in the Upper Hudson. Data from the MPI (1992) assessment was used to compare the 1976-1978 and 1994 inventories in this analysis because of the availability of PCB concentration data and *hot spot* area definitions (as scale drawings).
- The historical analyses assumed a solid specific weight (SSW) of 1 g/cc. Based on the low resolution core relationship between solid specific weight and total PCB concentration, estimates for SSW ranged from 0.5 to 0.79 g/cc for most 1976-1978 *hot spot* sample locations. Applying a SSW based on length-weighted average concentrations for 1976-1978 yielded about a 20 to 30 percent decrease in the original PCB inventory estimates.
- Sediment PCB data were shown to be log-normally distributed for both the 1976-1978 and 1994 data. The geometric mean, arithmetic mean, minimum variance, and unbiased estimates of the arithmetic mean were calculated to estimate and compare PCB inventories.
- Low resolution core samples were placed to define the *hot spot* area properties, not the smaller dredge location areas defined in MPI, 1992. The *hot spots* are the minimum area of PCB contamination for comparison between 1976-1978 and 1994 inventories.

- The low resolution core data provides the best estimate of the 1994 total PCB inventory. For the 1976-1978 inventory, the most accurate estimate is based on NYSDEC data provided in MPI, 1992. A comparison of these inventories indicate statistically significant loss of 50 to 80 percent for three *hot spots* (31, 34 and 37) relative to the 1976-1978 estimate, while *Hot Spot* 28 exhibited an apparent gain of 18 metric tons of total PCBs between 1976-1978 and 1994.
- Examination of the core profiles at *Hot Spot* 28 shows less than half of the sample locations have undergone deposition (burial). The remaining sites are either unchanged or have undergone scour based on the presence of the maximum total PCB concentration in the shallow sediment layer, as well as a net increase in shallow sediment concentration (six-fold) from 1976-1978 to 1994. The deposition history recorded by the high resolution cores indicates that this type of rise in shallow sediments can only be caused by scour. Between two and five percent of PCB mass was deposited between 1976-1978 and 1991 based on two dated high resolution cores collected from the upper Hudson below the TI Dam. The small increase in inventory in these cores makes such a large gain in inventory unlikely at *Hot Spot* 28. Since the high resolution cores are believed to represent continuous deposition, most of the gain at *Hot Spot* 28 probably results from an initial inaccurate assessment of the *Hot Spot* by the 1976-1977 sediment survey caused by too many shallow cores and grabs.
- *Hot Spot* 39 exhibits burial with total PCB concentrations much greater at depth. Compared to the Malcolm Pirnie, 1978 estimate (which used the entire core) there is not a significant change in inventory.
- Three areas appear unchanged (*Hot Spots* 25, 35 and dredge location 182) but only one (*Hot Spot* 25) has a sufficient number of samples to confirm the lack of change. Of the two remaining areas, *Hot Spot* 35 is better characterized.
- Deposition thickness varied considerably and consistently with PCB inventory gain and loss. The average depth of the maximum total PCB concentration for the low resolution cores is 18.7-inches (46.8-cm) in the *hot spots* exhibiting an apparent PCB inventory increase and 10.6-inches (26.5-cm) in the *hot spots* exhibiting loss. The difference in mean depth between areas of PCB loss and gain is statistically significant.

- *Hot Spots* 28 and 39 had large PCB inventories of 20 and 4 metric tons, respectively. The combined total is equivalent to the inventory of the entire Thompson Island Pool, estimated to be 23 metric tons by M. Brown *et al.*, 1988. Most of this mass (about 95 percent) was deposited prior to 1977, based on deposition histories developed from the high resolution cores.
- Because the low resolution cores can be assessed for completeness using both the core profiles and radionuclide information, the occurrence of sediment PCB inventory losses from the 1976-1978 sampling to the 1994 low resolution coring can be ascertained more definitively than can gains. Specifically, because the 1994 inventories are from cores that penetrated all recent sediments, it is probable that the entire current inventory has been captured. Therefore, the 1978 inventories may be underestimates. Thus, observed losses are minimum estimates and observed gains are maximum estimates.
- ^{137}Cs proved to be invaluable in assessing core completeness or near completeness, because the absence of ^{137}Cs in the bottom of the core was a reliable indicator that the core was complete.
- ^7Be occurrence showed a correlation with PCB inventory gain and loss on an area basis, but could not be proven to have a statistically significant relationship based on the 1976-1978 to 1994 inventory comparison.
- *Hot spot* boundaries appeared accurate, although in some instances *hot spot* areas needed to be increased to include all nearby areas of high contamination. Sonar image interpretation appears to provide some guidance as to regions of fine grain, higher contamination sediments.
- Comparison of the 1994 inventory with other estimates of the 1976-1978 inventory yield similar magnitude and direction of mass change in most instances. The MPI (1978) and Tofflemire and Quinn (1979) estimates took more of the deeper sediments into account. Thus, losses tended to be greater and gains smaller as compared to the MPI (1992) estimates of the 1976-1978 inventory. The mass change in *Hot Spot* 39 became an insignificant loss using the MPI (1978) estimates showing that some mass at depth was detected in the 1976-1978

sediment survey for this region. However, because the area used by MPI (1978) was much smaller than that for subsequent studies, the actual PCB quantity estimated was still much smaller than the 1994 estimate based on a larger *hot spot* area.

- The large apparent increases in PCB inventory in *Hot Spots* 28 and 39 are probably more related to underestimated PCB inventories in 1976 to 1978 (MPI, 1992) than to actual increases in PCB inventory since that time.
- Overall, sediments below the Thompson Island Dam exhibit both losses and gains. Losses totaled a minimum of 3.2 metric tons. Gains were estimated at 18.6 metric tons, but the actual gain in inventory is probably much less. Poor assessment of *Hot Spots* areas 28 and 39 in the 1976-1978 sediment survey caused by failure to capture what was apparently in place at the time of surveying yielded badly underestimated PCB inventories at these locations. Based on high resolution cores collected in the same area of the Upper Hudson, only a small percent of the 1994 mass was deposited between 1977 and 1991.
- These results show that the stability of the sediment deposits cannot be assured. It is likely that PCBs will continue to be released from the sediments. Burial of contaminated sediment by cleaner material is not occurring in most *hot spot* areas below the TI Dam. Burial of more PCB-contaminated sediment by less contaminated sediment has occurred in *Hot Spot* 39 and to a limited degree in *Hot Spot* 28. However, this process is limited and much of the other *hot spot* inventories has been re-released to the environment.

4.4.3 Sediment Contamination in the Near-Shore Environment

Sediments in the near shore environment were found to have higher PCB concentrations than originally estimated in the Phase 1 report. (TAMS/Gradient, 1991) Sediment concentrations upper 95% confidence interval for sediment concentrations based on the Low Resolution Coring samples ranged from 151 to 264 as compared to Phase 1 value of 66 mg/kg. The applicability of these results may be limited due to the small number of samples. These data will be considered in the preparation of the final human health risk assessment in Phase 2.

4.4.4 Summary

In this chapter, 1994 sediment inventories for the Upper Hudson have been compared with historical studies of the same river areas. Comparisons between the 1984 and 1994 sediment surveys for the Thompson Island Pool demonstrated the occurrence of statistically significant PCB losses from the sediment over the period 1984 to 1994. During this time approximately 39 percent of the inventory of sediments with PCB concentrations greater than 10 g/m² was lost. Of this loss, approximately 28 percent was the result of the re-release of PCB contamination from the sediment via scour or other sediment release processes. Both these estimates represent minimum estimates of the actual PCB losses. The remaining portion of the loss was attributed to dechlorination. The level of dechlorination noted was consistent with that obtained from the change in molecular weight of the PCB mixture as given in Chapter 3. Sediment inventories greater than 10 g/m² are associated with sediments with an average PCB concentration of 12 mg/kg and higher and peak concentrations of 50 mg/kg and higher.

Concurrent with this loss was the gain in PCB inventory among the less contaminated sediments (less than 10 g/m²). Inventories were estimated to have increased by 87 to 104 percent. This gain was attributed to input from upstream as well as the re-release of PCBs from the more contaminated sediment.

Examination of individually paired 1984-1994 sediment profiles found sites exhibiting inventory loss, inventory increase and lack of change. Inventory losses were the most commonly occurring condition, with some sites presenting indications of sediment scour. General burial of contaminated sediment by clean sediment was not apparent.

The comparison of the 1976-1978 and 1994 surveys for the areas below the TI Dam yielded similar conclusions. Of eight *hot spot* or dredge location areas studied, three exhibited inventory losses representing between 50 and 80 percent of the original inventory. Changes in three other areas could not be discerned. The remaining two areas exhibited apparent large gains which appeared to be the result of badly underestimated 1976-1978 PCB inventories and not the result of post-1978 deposition. One of these areas exhibited sediment burial although shallow sediments were still contaminated at the 5 mg/kg level. The other, more massive inventory associated with *Hot Spot 28* exhibited many core profiles suggesting PCB loss, probably via scour, based on the occurrence of the

highest PCB levels in the shallowest sediments. Thus, although the 1992 estimate for the PCB inventory at *Hot Spot* 28 was eleven-fold higher than the original 1976-1978 inventory estimate, coring evidence suggests that this area has been losing PCB inventory over time and that the 1976-1978 inventory was probably higher than the 1992 estimate.

In total, the low resolution coring survey achieved its goal of assessing current sediment PCB inventories and estimating inventory change since previous surveys. The results provide unequivocal evidence for the loss of PCBs from the sediment to the water column, supporting the contentions of the DEIR (TAMS, *et al.*, 1997). These results indicate that since 1984, a sediment PCB inventory loss has occurred, representing 28 percent of the PCB inventory from the more contaminated areas of the TI Pool. Similarly, since the 1976-1978 survey, a loss of about 3200 kg of PCBs has occurred from the *hot spots* below the TI Dam. In the meantime, the possibility of inventory gains in less contaminated areas of the river suggest that at least a portion of the re-release is serving to recontaminate other areas. Lastly, little evidence was found to suggest that burial of more contaminated materials with clean sediment was occurring on a widespread basis.

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